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Comprehensive two-dimensional gas chromatography using partial modulation via a pulsed flow valve with a short modulation period

Chris E. Freye[a], H. Daniel Bahaghighat[a,b], Robert E. Synovec[a,*]

[a] Department of Chemistry, Box 351700, University of Washington, Seattle, WA 98195, USA
[b] Department of Chemistry and Life Science, United States Military Academy, West Point, NY 10996, USA

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ABSTRACT

Partial modulation via a pulsed flow valve for comprehensive two-dimensional (2D) gas chromatography (GC × GC) is demonstrated, producing narrow peak widths, ^2W_b, on the secondary separation dimension, ^{2}D, coupled with short modulation periods, P_M, thus producing a high peak capacity on the ^{2}D dimension, ^2n_c. The GC × GC modulator is a pulse flow valve that injects a pulse of carrier gas at the specified P_M, at the connection between the primary, ^{1}D, column and the ^{2}D column. Using a commercially available pulse flow valve, this injection technique performs a combination of vacancy chromatography and frontal analysis, whereby each pulse disturbance in the analyte concentration profile as it exits the ^{1}D column results in data that is readily converted into a ^{2}D separation. A three-step process converts the raw data into a format analogous to a GC × GC separation, incorporating signal differentiation, baseline correction and conversion to a GC × GC chromatogram representation. A 115-component test mixture with a wide range of boiling points (36–372 °C) of nine compound classes is demonstrated using modulation periods of P_M = 50, 100, 250, and 500 ms, respectively. For the test mixture with a P_M of 250 ms, peak shapes on ^{2}D are symmetric with apparent ^2W_b ranging from 12 to 45 ms producing a ^2n_c of ~ 10. Based on the average peak width of 0.93 s on the ^{1}D separation for a time window of 400 s, the ^{1}D peak capacity is ^1n_c ~ 430. Thus, the ideal 2D peak capacity $n_{c,2D}$ is 4300 or a peak capacity production of 650 peaks/min using the P_M of 250 ms. Additionally, for a P_M of 50, 100 and 500 ms, the ^2n_c are 4, 7, and 12, respectively. Retention times on ^{2}D, ^2t_R, are reproducible having standard deviations less than 1 ms. Finally, the processed data is shown to be quantitative, with an average RSD of 4.7% for test analytes.

1. Introduction

Comprehensive two-dimensional (2D) gas chromatography (GC × GC) is a powerful technique for the analysis of complex samples containing analytes that are naturally volatile, semi-volatile, or amenable to gas phase analysis after derivatization [1–5]. Addition of a secondary separation dimension, ^{2}D, provides a 5-fold to 15-fold increase in total peak capacity over a one-dimensional (1D) separation (1D-GC). In order to transfer analytes from the primary ^{1}D column to the ^{2}D column, a modulation interface must be present. The modulator operates by injecting portions of the ^{1}D column effluent onto the ^{2}D column with a user defined, relatively rapid frequency. There are many types of modulators in GC × GC, but all fall under the three basic categories: thermal [1,6–15], valve-based [16–21], and flow modulation [22–29].

Thermal modulation relies on a low temperature to trap and focus analytes as they elute from the ^{1}D column and introduces them in a narrow pulse to the ^{2}D column through rapid heating. There are three types of thermal modulators: resistively heated trap [1,6,7], heated sweeper [8,9], and cryogenic focus, which is often divided into longitude movable trap [10] and jet trap [11–15]. Phillips and Liu developed the first thermal modulator using a slotted heater which swept across a thick-filmed capillary connecting the ^{1}D column to the ^{2}D column [1]. Analytes eluting from the ^{1}D column are retained in the thick film and then volatilized and injected onto the ^{2}D column when the heater sweeps over the capillary. The most common thermal modulator uses a cryogen to trap analytes before reinjecting them. Marriott and Kinghorn [10] pioneered the longitude movable cryogen trap, whereby a jet of fluid CO_2 is applied to produce a moving cryogenic trap with a small portion of capillary between the two columns. The condensed analytes are injected onto the ^{2}D column when the capillary is rapidly heated. Another cryogenic modulator, and perhaps the most commonly used thermal modulator, is the jet trap developed by Ledford and Billesbach [11], which uses strategically placed and timed jets of cryogenic gas or a combination of heat and cooled jets. Numerous improvements have been made to these thermal modulators.

Valve-based modulation commonly employs a diaphragm valve to

* Correspondence to: Department of Chemistry, University of Washington, Seattle, WA 98195-1700, USA.
E-mail address: synovec@chem.washington.edu (R.E. Synovec).

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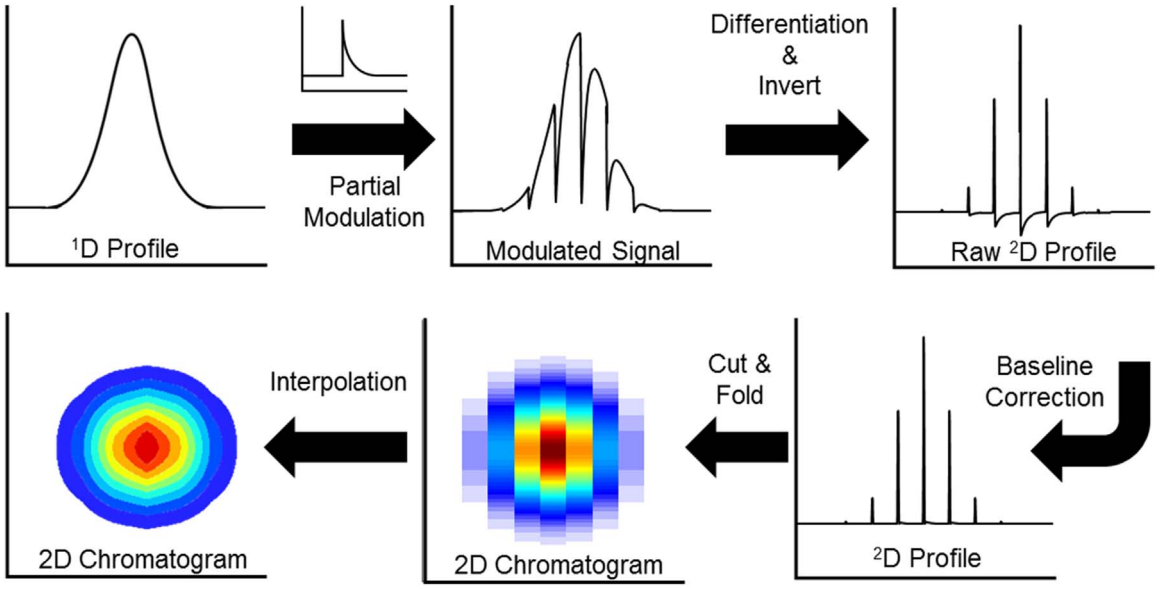

Fig. 1. Modulation process using the pulse flow valve and conversion of the modulated signal into a two-dimensional (2D) format with the appearance of a GC × GC chromatogram.

divert effluent from the ^{1}D to ^{2}D column [16]. The diaphragm valve utilized in the initial report had a temperature limit of 175 °C due to the temperature sensitive O-rings, and only ~ 10% of the effluent from ^{1}D column was injected onto the ^{2}D column. Improvements by Seeley increased detection sensitivity by employing a sample loop to collect the effluent from the ^{1}D separation before injection onto the ^{2}D column, with the fraction of the ^{1}D effluent transferred to the ^{2}D column approaching 100% [17]. Using a significantly higher flow rate on the ^{2}D column compared to the ^{1}D column, sample pulses are compressed within the sample loop creating narrow ^{2}D peaks while improving detection limits compared to 1D-GC [17,18]. The original temperature limit of 175 °C was overcome by face mounting the valve on the top of the GC, which extended the temperature limit to 265 °C [19]. Recent advances in diaphragm valve technology have extended the temperature limit to 325 °C with the valve mounted directly in the oven, avoiding the complication and shortcomings of face mounting the valve [18]. Diaphragm valve-based modulation has also been demonstrated to be compatible with mass spectrometry [20,21].

Flow modulation has its origins in Deans switching which is often used in heart-cutting GC-GC to transfer a portion of the effluent from the first GC column onto a subsequent GC column [22]. A Deans switch has been adapted by Seeley for use as a modulator for GC × GC [23]. Differential flow modulation is another type of flow modulation which closely resembles Deans switching, but results in total transfer of effluent from the ^{1}D column to the ^{2}D column. Differential flow modulation involves the alternation of filling and flushing cycles of a collection channel controlled by a solenoid valve [24]. Flow modulation is gaining popularity due to the operational simplicity, reliability, and capability to modulate components over a wide volatility range [22–28]. Flow modulation has also been demonstrated in an atypical manner. A pattern of the primary effluent is transferred to the secondary column instead of single pulses [29]. The detected signal is then deconvoluted and transformed into a GC × GC chromatogram. While extra processing is required to convert the detected signal into more readily interpretable data, more intense and narrower peaks are obtained compared to a traditional flow modulation technique.

Another interesting, yet unconventional, modulation approach was introduced by Cai and Stearns [30], a method referred to as “partial modulation.” Using a custom built pulse flow modulator, small pulses of carrier gas are repetitively injected at the interface between the ^{1}D and ^{2}D columns, creating either local high or low concentration pulses in the effluent departing the ^{1}D column, which are then separated on the ^{2}D column. Dependent upon the mode of modulation, either positive or negative “spikes” in analyte concentration are created. When the injected pulses are negative, the resulting ^{2}D separations are essentially performing vacancy chromatography. A modulation period, P_M, of 1 s was applied in this previous report. Since partial modulation produced raw data in an unconventional format, additional data processing is required to achieve a conventional appearing 2D plot of the GC × GC separation. The ^{2}D peak widths observed were ^2W_b ~ 50 ms and larger [30], similar to what is achieved by thermal [10–15], diaphragm valve [16–21,31], and standard flow modulation [23–28].

Partial modulation lends itself to producing a short P_M because the effluent from the ^{1}D column does not have to be cryogenically trapped or collected in a sample loop or channel. Moreover, there is no desorption or injection period, which facilitates very narrow peaks on the ^{2}D separation and thus a high ^{2}D peak capacity. While the initial report using partial modulation method was intriguing [30], there is untapped potential for producing extremely narrow ^{2}D peaks with ^2W_b smaller than 50 ms, and extremely short P_M. Being able to do so may open up new opportunities in the development of novel high speed versions of multi-dimensional GC-based separation technology involving “GC-sensors” [31–35].

In order to begin to explore these high speed GC-based technologies, herein we study the feasibility of a pulse flow valve modulator for GC × GC, implementing partial modulation using a commercially available pulse flow valve. Very short modulation periods are examined, P_M of 50, 100, 250 and 500 ms, with 50 and 100 ms notably shorter than the smallest P_M reported of 200 ms [31]. Using the commercially available pulse flow valve, this injection technique will be shown to perform a combination of vacancy chromatography and frontal analysis, whereby each pulse disturbance in the analyte concentration departing the ^{1}D column results in data that is readily converted into a ^{2}D separation. A procedure is introduced to convert the raw data obtained into the 2D form typical of a GC × GC separation. The basic concept is illustrated in Fig. 1, which shows the modulation of a single analyte using the commercial pulse flow valve and the subsequent conversion of the raw data into the typical 2D form of an analyte signal in a GC × GC chromatogram. The pulse flow valve creates pressure pulses in the shape of an exponentially modified Gaussian where the leading edge of each pressure pulse is extremely sharp and then slowly decays to zero. Negatively modulated signals are created as in vacancy chromatography, while also containing basic elements of a frontal analysis measurement. The raw data is differentiated to convert it into a