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Parallel comprehensive two-dimensional gas chromatography

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ABSTRACT

We introduce an information rich analytical approach called parallel comprehensive two-dimensional gas chromatography (2GC × 2GC). This parallel chromatography approach splits injected samples into two independent two-dimensional column ensembles and provides two GC × GC separations by using contra-directional thermal modulation. The first-dimension (^{1}D) and second-dimension (^{2}D) columns are connected using planar three-port microchannel devices, which are supplied with supplementary flow *via* two pressure controller modules. Precise carrier gas flow control at the junction of the ^{1}D and ^{2}D columns permits independent control of flow conditions in each separation column. The 2GC × 2GC approach provides two entirely independent GC × GC separations for each injection. Analysis of hop (*Humulus lupulus* L.) essential oils is used to demonstrate the capability of the approach. The analytical performance of each GC × GC separation in the 2GC × 2GC experiment is comparable to individual GC × GC separation with matching column configurations. The peak capacity of 2GC × 2GC is about 2 times than that of single GC × GC system. The dual 2D chromatograms produced by this single detector system provide complementary separations and additional identification information by harnessing different selectivity provided by the four separation columns.

1. Introduction

With the aim of providing enhanced qualitative information compared to conventional comprehensive two-dimensional gas chromatography (GC × GC), Savareear *et al.* introduced two closely related multiplexed GC × GC approaches utilising contra-directional thermal modulation [1,2]. Unlike other multi-column GC × GC methodologies [3–6], these multiplexed techniques employ a single detector to generate two two-dimensional (2D) separation windows for each injection within a single detector channel. Complementary separation and enhanced qualitative information were provided due to the selectivity differences between the different multiplexed stationary phase columns. By nature of the multiplexed approaches, a fast second-dimension (^{2}D) separation is especially important to avoid overlap of the two separation windows in the single chromatogram [1]. Therefore the investigators configured their setups by using relatively short (e.g. 0.4 m) and narrow internal diameter (e.g. 100 μm i.d.) ^{2}D columns coupled with conventional first-dimension (^{1}D) columns (i.e. 30 m × 250 μm i.d.) [2]. However, these ^{2}D column dimensions might not be the best choice for GC × GC analysis [7]. These ^{2}D columns lead to a considerably faster analysis, but at the expense of providing insufficient separation and band broadening due to overloading compared with longer and wider bore ^{2}D columns (e.g. 1 m × 250 μm i.d.).

Flow-mismatch between the two separation dimensions is a typical GC × GC problem stemming from the coupling of columns with considerably different internal diameter ^{1}D (regularly 250 μm) and ^{2}D columns (often 100 μm). This flow-mismatch can be resolved by adopting a wider ^{2}D column or by using ^{1}D and ^{2}D columns with the same internal diameter [5]. Flow conditions closer to optimal can be achieved in both dimensions, when columns with homologous internal diameter are used, leading to improved exploitation of the ^{2}D stationary phase selectivity and increased ^{2}D sample capacity [7–9]. A recent study has experimentally demonstrated that the use of homologous column diameter in both dimensions can substantially reduce the detrimental effect

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on underutilisation of the primary peak capacity (^1U) compared to that of comparatively narrow ^{2}D column. Employing homologous column diameters in both separation dimensions is one of the key factors enabling a near-theoretical maximum in peak capacity gain (G_n) [10].

In the present investigation we employed a simple but effective method of independently controlling carrier-gas flow in the first- and second-dimensions. Recently, Luong *et al.* utilised auxiliary flow control between the ^{1}D and ^{2}D columns for the purpose of *Retention Time Locking* and *Back-Flushing* in GC × GC [11]. Similarly, changing the carrier-gas pressure at the junction of two series-coupled capillary GC columns has been reported as a versatile approach to achieve the best possible separation of multicomponent mixtures [12–14]. By changing the junction pressure, it is able to alter the relative retention position of components, and therefore adjust the selectivity of the column ensemble leading to optimal separation. Independent control of flow conditions also greatly assists development of multi-column GC × GC approaches. To this end, we introduce a four-column multiplexed technique with two independent ^{1}D columns each coupled to its own ^{2}D column, and employ an additional gas supply and precise electronic pressure control at the midpoint between the two dimensions. Comparison of analyses with and without independent ^{2}D flow control are made using otherwise matching column sets and the importance of applying flow control to adjust the separation speed in ^{2}D is outlined. The capability of independent flow controlled 2GC × 2GC is demonstrated by the analyses of hop (*Humulus lupulus* L.) essential oil with two column combinations comprising non-polar × polar and polar × non-polar column sets. Important features of the proposed independent flow controlled 2GC × 2GC approach compared to multiplexed approaches introduced by Savareear *et al.* are discussed.

2. Experimental

2.1. Chemicals and reagents

Hop (*Humulus lupulus* L.) essential oil was prepared by hydrodistillation of dried hop cones (Hop Products Australia, North Hobart, Australia), and was diluted (1:20, v/v) in dichloromethane (Sigma-Aldrich, Castle Hill, Australia) prior to GC analyses.

2.2. Instrumentation and experimental conditions

All analyses were performed using a Leco GC × GC-FID instrument with an LN2 Cooled Thermal Modulator (LECO Australia, Castle Hill, Australia). The chromatograph was equipped with a split/splitless injector, operated with a 20:1 split ratio and inlet temperature of 200 °C. A 1 μL sample volume was injected. Hydrogen carrier-gas was supplied using a Parker Balston H2PEM-260 generator (Parker Hannifin, Castle Hill, Australia). Effluent from each secondary column was monitored by a single flame ionization detector (FID) operated at 100 Hz and 250 °C. Data were collected and processed using Leco ChromaTOF software.

2.3. GC × GC with independent flow control

Independently flow controlled GC × GC analyses were performed by using two different column combinations. A 60 m × 250 μm i.d. × 0.25 μm d_f SGE BPX5 column was used as the ^{1}D column, and a 1.2 m × 250 μm i.d. × 0.25 μm d_f SGE SolGel-Wax column was used as the ^{2}D column. The two columns were connected using a SilFlow 3-port micro channel device (Trajan Scientific and Medical, Ringwood, Australia). The ^{2}D column was installed in the regular configuration through the GC × GC modulator and secondary oven. An auxiliary pressure controller module (PCM; Agilent Technologies, Mulgrave, Australia) was connected to the central port of the SilFlow device with 1.1 mm outside diameter SilFlow stainless steel capillary tubing sleeved to 1/16" at one end for connection to the PCM. A schematic diagram of the system is shown in Fig. 1. Carrier-gas flow rate in ^{1}D was set at 2.5 mL/min; while ^{2}D carrier-gas flow rate was set at 2.5 mL/min. The primary oven temperature program was 50 °C (1.1 min hold) to 245 °C (0.9 min hold) ramped at 3.5 °C/min. The ^{2}D column offset was set at +15 °C from the primary oven, and modulator temperature offset was set at +25 °C relative to the secondary oven. The modulation period was of 2.0 s (hot pulse of 0.6 s) was used throughout. Another column combination comprising a 60 m × 250 μm i.d. × 0.25 μm d_f SGE SolGel-Wax column and 1.2 m × 250 μm i.d. × 0.25 μm d_f SGE BP10 was operated using the same conditions described above. All separation columns were from Trajan Scientific and Medical.

2.4. GC × GC without independent flow control

GC × GC analyses without independent flow control were performed using the column combinations and conditions described in Section 2.3, except that the ^{1}D and ^{2}D columns were connected directly using press-tight connectors (Restek Corporation, Bellefonte, PA). The carrier-gas flow rate was set at 2.5 mL/min for all experiments.

2.5. 2GC × 2GC with independent flow control

Independently flow controlled multiplexed 2GC × 2GC analyses were achieved by using contra-directional modulation. Two parallel ^{2}D columns were installed contra-directionally in the GC × GC modulator. All 2GC × 2GC analyses were performed by splitting the flow from the inlet into two ^{1}D columns by means of a twin-hole graphite ferrule (Trajan). The two ^{1}D columns used were: $^1D_1$ (A) SGE BPX5 60 m × 250 μm i.d. × 0.25 μm d_f; $^1D_2$ (B) SGE SolGel-Wax 60 m × 250 μm i.d. × 0.25 μm d_f. Each ^{1}D column was connected to one ^{2}D column using a SilFlow 3-port microchannel device, and two PCMs were connected to the central port of each SilFlow device. The two ^{2}D Columns used were: $^2D_1$ (C) SGE BP10 1.2 m × 250 μm i.d. × 0.25 μm d_f; $^2D_2$ (D) SGE SolGel-Wax 1.2 m × 250 μm i.d. × 0.25 μm d_f. Flow from the two ^{2}D columns was directly passed into a single FID by means of a twin hole graphite ferrule. For convenience of column installation and operation, the secondary oven was removed from the 2GC × 2GC system. All four columns were heated using the main GC oven. An instrument schematic of the multiplexed independently flow controlled 2GC × 2GC analytical system is illustrated in Fig. 2. The carrier-gas flow rate used in ^{1}D was 1.2 mL/min; while the ^{2}D carrier-gas flow rate used was 2.5 mL/min. To maintain appropriate separation space between the two separation windows in the chromatogram the total modulation period used was 4.0 s (hot pulse 1.6 s). The oven temperature program used was 50 °C (1.1 min hold) to 245 °C (0.9 min hold) ramped at 3.5 °C/min. The modulator temperature offset was set at +15 °C.

2.6. 2GC × 2GC without independent flow control

Multiplexed 2GC × 2GC analyses without independent flow control were performed by using two sets of column combinations. The first column set used was the same as the independently flow controlled 2GC × 2GC experiments. Total carrier-gas flow rate was set at 2.5 mL/min. Another column set used comprised a 60 m × 250 μm i.d. × 0.25 μm d_f SGE BPX5 ^{1}D column with a 0.45 m × 100 μm i.d. × 0.1 μm d_f Rtx-Wax ^{2}D column along with a 60 m × 250 μm i.d. × 0.25 μm d_f SGE SolGel-Wax ^{1}D column with