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Adaptive Two-Dimensional Microgas Chromatography

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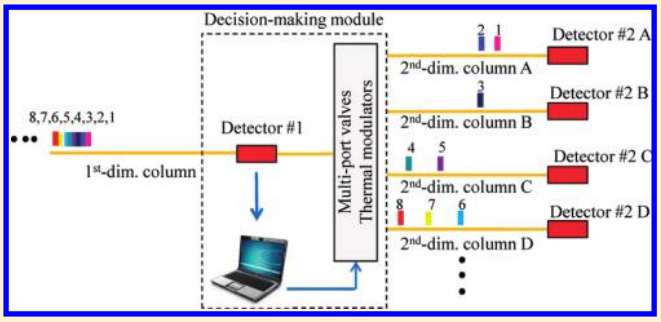
Supporting Information

ABSTRACT: We proposed and investigated a novel adaptive two-dimensional (2-D) microgas chromatography system, which consists of one 1st-dimensional column, multiple parallel 2nd-dimensional columns, and a decision-making module. The decision-making module, installed between the 1st- and 2nd-dimensional columns, normally comprises an on-column nondestructive vapor detector, a flow routing system, and a computer that monitors the detection signal from the detector and sends out the trigger signal to the flow routing system. During the operation, effluents from the 1st-dimensional column are first detected by the detector and, then, depending on the signal generated by the detector, routed to one of the 2nd-dimensional columns sequentially for further separation. As compared to conventional 2-D GC systems, the proposed adaptive GC scheme has a number of unique and advantageous features. First and foremost, the multiple parallel columns are independent of each other. Therefore, their length, stationary phase, flow rate, and temperature can be optimized for best separation and maximal versatility. In addition, the adaptive GC significantly lowers the thermal modulator modulation frequency and hence power consumption. Finally, it greatly simplifies the postdata analysis process required to reconstruct the 2-D chromatogram. In this paper, the underlying working principle and data analysis of the adaptive GC was first discussed. Then, separation of a mixture of 20 analytes with various volatilities and polarities was demonstrated using an adaptive GC system with a single 2nd-dimensional column. Finally, an adaptive GC system with dual 2nd-dimensional columns was employed, in conjunction with temperature ramping, in a practical application to separate a mixture of plant emitted volatile organic compounds with significantly shortened analysis time.



Microgas chromatography (μGC) has attracted tremendous research interest due to its wide applications in areas such as environmental protection,[1,2] biomedical diagnostics,[3,4] industrial monitoring and occupational safety,[5] homeland security, and the battlefield.[6−8] As compared to the conventional benchtop GC, μGC offers a compact size, a lightweight, and the ability to conduct rapid, on-site vapor analysis. However, μGC achieves these advantages at the expense of separation capability, which is one of the most important features of a GC system in analyzing complex gas mixtures. This loss of separation capability is due primarily to the shortened length of the separation columns used. To date, a number of methods have been developed to address this challenge,[2,9−19] among which comprehensive two-dimensional GC (or 2-D GC) technology is the best and most widely used solution. This technology utilizes two GC columns connected in series and coated with different stationary phases.[12,13,15,19] A modulator is installed between the two GC columns. It collects the effluent from the 1st-dimensional column, focuses it into a very narrow band, and then reinjects it into the 2nd-dimensional column for additional separation. Since analytes undergo two independent separations, they can be differentiated from each other on a 2-D chromatogram by the retention time in the 1st- and the 2nd-dimensional column.

Despite the significantly improved separation capability, existing 2-D GC technology faces several challenges. (1) Since the modulator has to continuously cut and send the effluent from the 1st-dimensional column to the 2nd-dimensional column at a high frequency, the separation at the 2nd-dimensional column needs to be finished within only a few seconds before the modulator injects the next effluent to the 2nd-dimensional column, which greatly limits the separation

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capability of the 2nd-dimensional column. (2) High frequency operation of the modulator consumes a considerably large amount of power, which is not suitable for portable instruments such as those used for on-site gas analysis or in remote distributed gas surveillance/monitoring. (3) Very precise synchronization is required between the modulator and vapor detector at the terminal end of the 2nd-dimensional column. Failure in synchronization may cause a serious problem in data reconstruction. (4) 2-D GC generates a much larger amount of data than 1-D GC, making the data analysis extremely complicated and challenging.[20]

In this work, we proposed and investigated a concept of adaptive 2-D μGC that provides better, more flexible, and more adaptable separation and simplified 2-D chromatogram reconstruction. As illustrated in Figure 1, this system consists

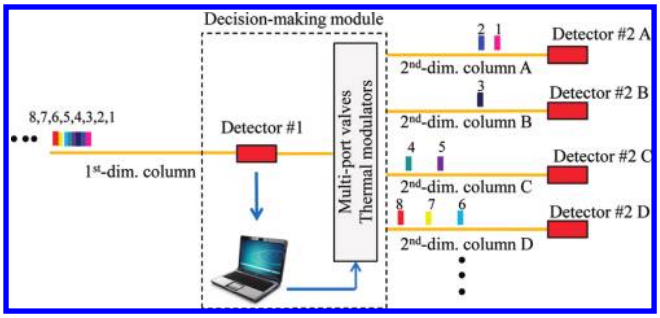

Figure 1. Conceptual illustration of the adaptive parallel 2-D GC system. It consists of one 1st-dimensional column, multiple parallel 2nd-dimensional columns, and a decision-making module installed between the 1st- and 2nd-dimensional columns. The decision-making module normally comprises an on-column nondestructive vapor detector (such as Detector #1), a flow routing system (such as multiport valves and thermal modulators), and a computer that monitors the detection signal from the detector and sends out the trigger signal to the flow routing system.

of one 1st-dimensional column, multiple parallel second columns, and a decision-making module installed between the 1st- and 2nd-dimensional columns. The decision-making module normally comprises an on-column nondestructive vapor detector (Detector #1 in Figure 1), a flow routing system (such as multiport valves and thermal modulators), and a computer that monitors the detection signal from the detector and sends out the trigger signal to the flow routing system. Since all columns are independent of each other, this system can be called 1×N 2-D GC, where N is the number of the 2nd-dimensional columns.

During operation, Detector #1 monitors the effluents from the 1st-dimensional column, providing the 1st-dimensional retention time and the information for the decision-making module to decide which 2nd-dimensional column the effluent should be routed to and when the thermal modulator should be turned on. After the entire effluent peak coming out of the 1st-dimensional column is trapped by the thermal modulator, the thermal modulator is turned on and the entire trapped effluent is then sent to the 2nd-dimensional column for further separation, which can be detected by Detector #2. The decision-making module may also contain a timing system or receive feedback from Detector #2 in order to determine whether a 2nd-dimensional column is busy (i.e., separation is still ongoing) or available (i.e., separation is complete). If all 2nd-dimensional columns are busy, the flow in the 1st-dimensional column is halted. To increase the versatility and to optimize the separation capability of the proposed adaptive μGC system, the 2nd-dimensional columns can use different lengths, stationary-phase coatings, flow rates, and temperatures.

The adaptive 2-D μGC proposed in this paper has a number of unique and advantageous features. (1) The on-column detector (Detector #1 in Figure 1) detects the analytes eluted from the 1st-dimensional column, which not only records the analytes' retention time at the 1st-dimensional column but also triggers the flow routing system to focus and reinject an entire effluent peak containing one or several analytes into the 2nd-dimensional column. Therefore, the time interval between the two adjacent injections becomes very flexible and can be adjusted for each injection. Consequently, a longer 2nd-dimensional column can be used to increase its separation capability, resulting in improved resolution in the 2nd-dimensional column. (2) Multiple 2nd-dimensional columns allow effluents from the 1st-dimensional column to be distributed to different 2nd-dimensional columns. It is possible to use different 2nd-dimensional columns with various lengths, coatings, flow rates, and temperatures for best separation and maximal versatility. (3) The flow routing system works only when it is triggered by the on-column detector at the end of the 1st-dimensional column, instead of working at a high frequency during the whole analysis process, which can significantly reduce the power consumption. This feature is particularly attractive when the μGC is used in remote distributed gas surveillance/monitoring. (4) The adaptive 2-D μGC lowers the requirements for timing and synchronization. (5) Injection of the entire eluted peak coming out of the 1st-dimensional column into the 2nd-dimensional column avoids cutting it into several fractions as in conventional 2-D GC so that the recorded retention time of each peak can be directly used to reconstruct the 2-D chromatogram, thus eliminating complex postdata processing. It should be noted that multiple parallel 2nd-dimensional columns described here are also used in 2-D liquid chromatography (LC) systems.[21−28] However, all the 2nd-dimensional columns in the LC system need to be exactly the same (stationary phase, length, temperature, and flow rate, etc.) in order to reconstruct the 2-D chromatogram.[29] A 2-D GC system with two different 2nd-dimensional columns has also been reported, where the effluent from the 1st-dimensional column is equally split into the two 2nd-dimensional columns.[30,31] Although this 2-D GC system produces a pair of 2-D chromatograms for each run and thus enhances the GC separation efficiency and sample identification capability, it suffers from the potential loss of samples for each 2nd-dimensional column and more complicated 2-D chromatogram reconstruction processes and data analysis. Furthermore, the maximal time available for separation on the 2nd-dimensional column is still limited by the thermal modulator modulation frequency (approximately 0.2−1 Hz).[30,31] Recently, another 2-D GC design was demonstrated by diverting part of effluents from the 1st-dimensional column to an off-column detector for direct measurement of the 1st-dimensional retention time.[32] Again, it encounters the same or similar aforementioned drawbacks (such as loss of samples).

In this paper, we demonstrated the feasibility of this adaptive 2-D GC concept using conventional macro-scale components in two examples: an adaptive GC system with a single 2nd-dimensional column (see Figure 2A) and with dual 2nd-dimensional columns (see Figure 2B). Details of these systems will be described in the subsequent sections. *However, we would like to emphasize that the adaptive 2-D GC concept and the*

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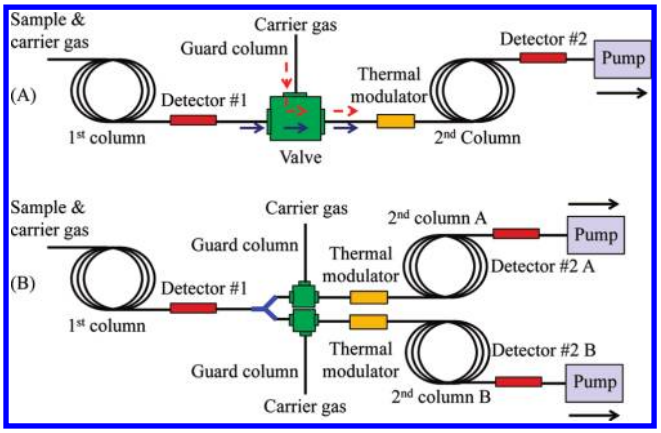

Figure 2. Schematic of embodiments of the proposed adaptive 2-D μGC. (A) Shows the adaptive 2-D μGC with a single 2nd-dimensional column. Solid arrows represent the flow direction when system works in Step 1, whereas dashed arrows represent the flow direction when the system works in Steps 2 and 3. (B) Schematic of 2-D μGC with dual 2nd-dimensional columns. A Y-connector connected both 2nd-dimensional columns to the 1st-dimensional column. A valve was installed for each of the 2nd-dimensional columns. In this manner, the effluents from the 1st-dimensional column were sent to the two 2nd-dimensional columns alternately, significantly shortening the overall analysis time. Note that only when both 2nd-dimensional columns were busy would the flow in the 1st-dimensional column be suspended until at least one of the 2nd-dimensional columns became available.

operation/detection principle presented here are applicable to any GC systems regardless of separation columns, detectors, and decision-making modules used in the system.

MATERIALS AND METHODS

Materials. All the analytes used in the experiment were purchased from Sigma (St. Louis, MO) and had purity greater than 97%. RTX-1 (part no. 10105, inner diameter (i.d.) = 250 μm) and guard columns (part no. 10000, i.d. = 250 μm) were purchased from Restek (Bellefonte, PA). HP-5 (part no. 19091J-413) was purchased from Agilent Technologies Inc. (Santa Clara, CA). Carbowax-coated GC column (part no. 24077, i.d. = 250 μm) was purchased from Sigma. Universal quick seal column connectors (part no. 23627) and Universal angled "Y" connectors (part no. 20403-261) were purchased from Sigma and Restek, respectively. Single-mode fibers (SMF-28) were purchased from Corning (Corning, NY). All materials were used as received.

Experimental Setup. To implement the adaptive 2-D GC concept, we employed an experimental setup illustrated in Figure 2A,B. In the single 2nd-dimensional column system (Figure 2A), the 1st-dimensional column was coated with RTX-1 or HP-5 (coating thickness was 200 nm), whereas the 2nd-dimensional column was coated with Carbowax (coating thickness was 200 nm). The two columns were connected through a decision-making module, which consisted of an on-column nondestructive detector (Detector #1), a three-port valve (Parker, part no. 009-0269-900), a thermal modulator, and a computer. Detector #1 was an optical fiber based Fabry-Pérot vapor sensor developed in our lab.[16,33,34] It could be installed inside a GC column in a manner that did not interfere with the gas flow while nondestructively detecting the vapor eluted out from the 1st-dimensional column. A chromatographic peak recorded by Detector #1 indicated the passage of an effluent, which was later trapped by a customized thermal modulator installed after Detector #1. The modulator was made of a quartz tube (i.d. = 2 mm, length = 2 cm) packed with 6 mm long sorbent bed (Carbopack B and Tenax TA). An electrical coil was wrapped into a cylindrical shape (i.d. = 1.5 cm, length = 1 cm) to cover the outer surface of the modulator for heating. Another detector (Detector #2, which was the same as Detector #1) was installed at the end of the 2nd-dimensional column. A mini-diaphragm pump (Parker, part no. D713-22-01) was placed at the end of the system to provide the flow. All connections between two components were through a press-tight column connector.

The operation procedures can be divided into the following three steps: (Step 1) The valve connected the 1st- and 2nd-dimensional column. The effluent eluted from the 1st-dimensional column was detected by Detector #1. Then, it passed through the valve and was trapped by the thermal modulator. When a chromatographic peak detected by Detector #1 returned back to the baseline, indicative of complete passage of the effluent, a signal was generated from the computer to trigger the flow routing system (the three-port valve and the thermal modulator in this particular case). (Step 2) After being triggered, the valve connected the 2nd-dimensional column to the carrier gas directly. The 1st- and 2nd-dimensional columns were disconnected, and the flow of analytes in the 1st-dimensional column was stopped. Meanwhile, the modulator was heated from room temperature to 300 °C within 3 s, reinjecting the trapped effluent into the 2nd-dimensional column. As soon as its temperature reached 300 °C, the modulator was naturally cooled down to room temperature (in about 30 s) to trap the next effluent from the 1st-dimensional column. (Step 3) Further separation took place in the 2nd-dimensional column. Detector #2 detected the separated peak(s) at the 2nd-dimensional column and recorded their elution time. Upon the completion of separation (or after preset time lapse), the valve reconnected the 1st- and the 2nd-dimensional columns and Step 1 was resumed.

The dual 2nd-dimensional column system (Figure 2B) added another independent 2nd-dimensional column to the 1st-dimensional column via a "Y" connector. Each column (1st-dimensional column, 2nd-dimensional column A and B) had a detector installed at its end. A mini diaphragm pump was attached to each of the 2nd-dimensional columns. The overall operation procedures were similar to those for the single 2nd-dimensional column system described above. Initially, the 2nd-dimensional column A was connected to the 1st-dimensional column whereas the 2nd-dimensional column B was disconnected from the 1st-dimensional column. When an effluent passed from the 1st-dimensional column, it was routed to the 2nd-dimensional column A, which was subsequently disconnected from the 1st-dimensional column. Meanwhile, the 2nd-dimensional column B was connected to the 1st-dimensional column to accommodate the following effluent. In this manner, the effluents from the 1st-dimensional column were sent to the two 2nd-dimensional columns alternately, significantly shortening the overall analysis time. Note that only when both 2nd-dimensional columns were busy would the flow in the 1st-dimensional column be suspended until at least one of the 2nd-dimensional columns became available.

Measurements. Gas analyte was extracted from the head space of the bottle containing the analyte by a solid-phase microextraction (SPME) fiber (PDMS/DVB, 65 μm diameter fiber, Supelco 57310-U) and was injected through the GC injector (Varian 3800, heated to 250 °C), which was connected

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to the 1st-dimensional column. The head pressure of the GC injector was set to zero. Gas analytes and ultrahigh purity (UHP) helium (used as carrier gas) were drawn into the system by the mini-diaphragm pump. To maintain a constant flow rate of 1 mL/min at both 1st- and 2nd-dimensional columns, an additional column with the same dimensions (i.d. and length) as the 1st-dimensional column was attached to the upstream of each 2nd-dimensional column via the three-port valve (see Figure 2A,B). All the components were kept at room temperature, unless otherwise noted. A customized LABVIEW program was used to monitor signals from detectors in real-time, and the data was recorded at a rate of 20 Hz.

RESULTS AND DISCUSSION

Single 2nd-dimensional Column System. The feasibility and working principle of the proposed adaptive 2-D μGC system are well illustrated by separating a mixture of five analytes in Figure 3. The mixture sample was gradually

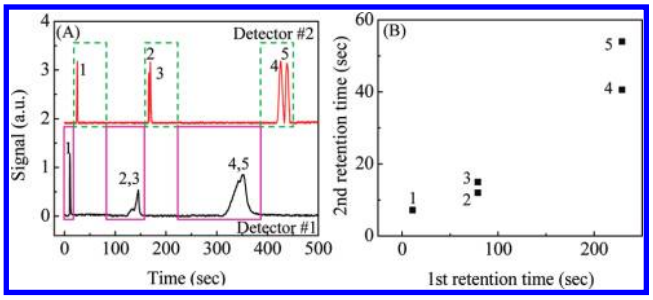

Figure 3. 2-D separation results obtained from the adaptive μGC system illustrated in Figure 2A. (A) Chromatograms from Detector #1 and #2. Solid and dashed boxes represent the separation at the 1st- and 2nd-dimensional column, respectively. Spaces outside the solid and dashed boxes represent the durations when separation was suspended at the 1st- and 2nd-dimensional column, respectively. Analyte #2 and #3 and Analyte #4 and #5 were coeluted from the 1st-dimensional column and were detected by Detector #1. They were clearly separated by the 2nd-dimensional column and detected by Detector #2. The beginning (end) time of the solid boxes were 0 s (20 s), 80 s (154 s), and 214 s (385 s). The beginning (end) time of the dashed box was the same as the end (beginning) time of the preceding (following) solid box. The duration of the dashed boxes was 60 s to ensure that all the analytes in the 2nd-dimensional column were eluted. (B) The corresponding 2-D chromatogram. Analytes: 1, pentane; 2, nonane; 3, 1-hexanol; 4, decane; 5, cis-3-hexenyl acetate. The first column was 1.5 m long and was coated with RTX-1. The 2nd-dimensional column was 0.8 m long and was coated with Carbowax. The retention time of a peak is measured at its apex. Curves in (A) are vertically shifted for clarity.

separated as it traveled in the first column until Detector #1 detected the first eluted peak. When the signal of Detector #1 returned back to the baseline, indicating that the eluted analyte(s) had passed through the 1st-dimensional column and was trapped by the thermal modulator, the valve was switched to disconnect the 1st-dimensional column from the 2nd-dimensional column so that the separation in the 1st-dimensional column was suspended. Meanwhile, the thermal modulator was heated up to 300 °C to release the trapped analyte(s) in a sharp peak for further separation in the 2nd-dimensional column. In order to ensure the completion of the separation at the 2nd-dimensional column, a 60 s operation time was applied to the 2nd-dimensional column before switching the valve back to reconnect the 1st- and 2nd-dimensional column. After reconnection, the separation at the 1st-dimensional column resumed until Detector #1 detected the second eluted peak, and then, the separation and detection cycle continued as described above.

The corresponding chromatograms obtained from Detector #1 and #2 are shown in Figure 3A. The total analysis time was approximately 450 s, which was mainly determined by the retention time of the last analyte at the 1st-dimensional column (approximately 230 s for the case in Figure 3; Note: an extra 40 s was needed for the last analyte to *completely* elute out of the 1st-dimensional column) and the sum of all of the operation time at the 2nd-dimensional column (approximately 180 s for the case in Figure 3). During the above procedures, whenever the 2nd-dimensional column was in operation, the flow in the 1st-dimensional column was suspended, thus adding to the overall analysis time. The analysis time can certainly be shortened significantly by implementing multiple 2nd-dimensional columns, which will be discussed in detail later. The 2-D chromatogram of the mixture is presented in Figure 3B. The detailed calculation of the retention time at each column is discussed in the Supporting Information.

The strong separation capability and simple data processing merit of the proposed system were further demonstrated by an analysis of a mixture of 20 analytes with various volatilities and polarities. As shown in the chromatograms from Detector #1 and #2 (Figure 4A), although there were eight coelution peaks occurring in the 1st-dimensional column, all 20 analytes were well separated by the 2nd-dimensional column. The 2-D chromatogram is presented in Figure 4B, having the longest retention time at the 1st- and 2nd-dimensional column of approximately 500 and 80 s, respectively. Note that, although the retention time of the last coelution peak in the 2nd-dimensional column exceeded the 60 s operation time, the system was able to adapt itself to extend the operation time until Detector #2 detected the analyte(s). This capability is not obtainable with conventional 2-D GC systems, whose separation time at the 2nd-dimensional column is fixed and is determined by the operation frequency of the modulator (usually 0.1−1 Hz). The total analysis time was approximately 1200 s, longer than 580 s (~500 s in the 1st-dimensional column and ~80 s in the 2nd-dimensional column) if a conventional 2-D GC system had been used to separate the same mixture under the same experimental conditions. Once again, this long analysis process was limited mainly by the use of a single 2nd-dimensional column, because the separation at the 1st-dimensional column had to be suspended until the separation at the 2nd-dimensional column was completed. By implementing multiple parallel second columns, the analysis time is expected to be significantly shorter.

Dual 2nd-Dimensional Column System. A 2-D GC system with dual 2nd-dimensional columns was demonstrated as the simplest illustration of the multiple parallel 2nd-dimensional column system. The system is capable of delivering the eluted peaks from the 1st-dimensional column to one of the parallel 2nd-dimensional columns, whichever is available (or at the stand-by mode). Only when both 2nd-dimensional columns are busy (i.e., in operation) will the separation at the 1st-dimensional column be suspended until at least one of the 2nd-dimensional columns becomes available. In this analysis, the same mixture of 20 analytes was tested and the analysis results are shown in Figure 5A,B. The operation time for each 2nd-dimensional column was set to be 30 s but could certainly be shortened or extended if needed, as discussed previously.

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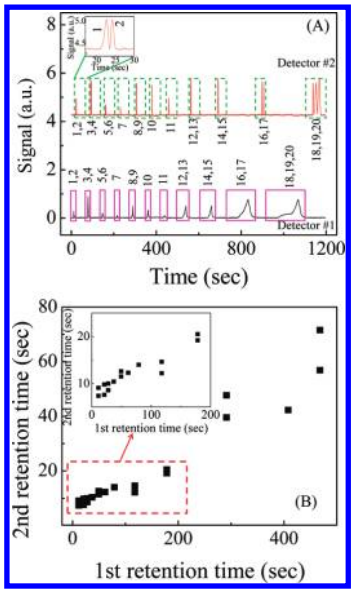

Figure 4. 2-D separation results of 20 analytes obtained from the adaptive 2-D μGC system shown in Figure 2A. (A) Chromatograms from Detector #1 and #2. Solid and dashed boxes represent the separation at the 1st- and 2nd-dimensional column, respectively. Spaces outside the solid and dashed boxes represent the durations when separation was suspended at the 1st- and 2nd-dimensional column, respectively. All analytes were resolved by Detector #2. Inset is the enlarged peaks of Analyte #1 and #2 detected by Detector #2. (B) The corresponding 2-D chromatogram extracted from (A). Analytes: 1, pentane; 2, acetic acid; 3, chlorotrimethysilane; 4, heptane; 5, pyridine; 6, 1-propanol; 7, 1-butanol; 8, tetramethyl orthosilicate; 9, octane; 10, cis-3-hexen-1-ol; 11, trans-2 hexenal; 12, nonane; 13, 1-hexanol; 14, tetraethyl orthosilicate; 15, limonene; 16, decane; 17, cis-3-hexenyl acetate; 18, undecane; 19, 1-octanol; 20, diethyl methyl-phosphonate. The 1st-dimensional column was 2 m long and was coated with RTX-1. The 2nd-dimensional column was 0.8 m long and was coated with Carbowax. The retention time of a peak is measured at its apex. Curves in (A) are vertically shifted for clarity.

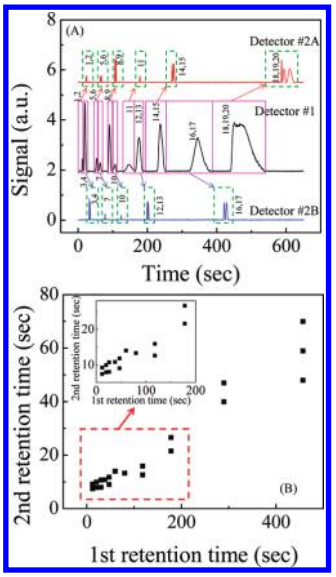

Figure 5. 2-D separation results of 20 analytes obtained from the adaptive 2-D μGC system shown in Figure 2B. (A) Chromatograms from Detector #1, #2A, and #2B. Solid and dashed boxes represent the separation at the 1st- and 2nd-dimensional column, respectively. Spaces outside the solid and dashed boxes represent the durations when separation was suspended at the 1st- and 2nd-dimensional column, respectively. All analytes were resolved by Detector #2A and #2B. (B) The corresponding 2-D chromatogram extracted from (A). Analytes were the same as in Figure 4. The 1st-dimensional column was 2 m long and was coated with RTX-1. The two 2nd-dimensional columns were 0.8 m long and were coated with Carbowax. The retention time of a peak is measured at its apex. Curves in (A) are vertically shifted for clarity.

Compared to the single 2nd-dimensional column system, the dual 2nd-dimensional column system has the same high chromatographic resolution but significantly shortened analysis time of approximately 650 s (the calculation of the retention time at the 1st- and 2nd-dimensional column can be found in the Supporting Information). Since the minimum analysis time was determined by the retention time of the last analyte eluted out from the 1st-dimensional column (~500 s), the added analysis time by the 2nd-dimensional column was only around 150 s, which is close to the added analysis time in a conventional 2-D GC system (~80 s) and about 4.6 times shorter than in the single 2nd-dimensional column system (~700 s). Note that the above ~150 s were mainly caused by the very short suspension time on the first column when both second columns were busy. If enough parallel second columns are installed so that the separation at the 1st-dimensional column does not have to be suspended, the added analysis time caused by the 2nd-dimensional separation is expected to be the same as in a conventional 2-D GC system.

We further employed the adaptive 2-D GC system in one practical application to analyze plant emitted volatile organic compounds (VOCs) mixed with alkanes and toluene. Plants release VOCs in response to many environmental stimuli, and volatile emission "signatures" can provide highly specific information with broad applications for use in agriculture and defense.[35,36] For demonstration purposes, we used commercially available standards to mimic the actual emission of plants. The analysis results are shown in Figure 6A,B. During the operation, the entire 1st-dimensional column was placed into a GC oven for temperature ramping to accelerate the elution of heavy analytes. During the ramping, the oven was kept at room temperature for 3 min and then heated up to 150 °C at a rate of 20 °C/min. All other components remained at room temperature. The operation time for each 2nd-dimensional column was initially set to be 20 s for separation of fast effluents. It was extended up to nearly 200 s during the later stage of separation to accommodate slow effluents (see, for example, Analyte #14–#18). The total analysis time was 1270 s, of which the 1st-dimensional column analysis time was 1100 s and the added analysis time resulting from the 2nd-dimensional column was only 170 s. Figure 6 clearly showcases the advantages of the adaptive 2-D GC in comparison with the conventional 2-D GC that usually encounters increasing challenges when dealing with analytes that have long 2nd-dimensional retention times (e.g., ~180 s for Analyte #14). In addition, the thermal modulator was turned on/off only 13 times, which led to nearly 100-fold reduction in modulator power consumption, as compared to the conventional 2-D GC with a modulation frequency of 1 Hz.

CONCLUSION AND FUTURE WORK

We have proposed and demonstrated a novel adaptive 2-D GC system that consists of a 1st-dimensional column, multiple parallel 2nd-dimensional columns, and a decision-making

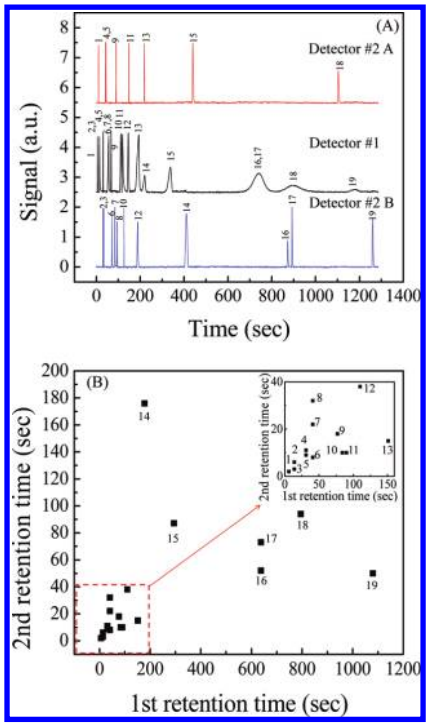

Figure 6. 2-D separation results of plant emitted VOCs mixed with alkanes and toluene using the adaptive 2-D μGC system shown in Figure 2B. (A) Chromatograms from Detector #1, #2A, and #2B. All analytes were resolved by Detector #2A and #2B. (B) The corresponding 2-D chromatogram extracted from (A). Analytes: 1, pentane; 2, heptane; 3, dimethyl disulfide; 4, octane; 5, toluene; 6, pinene; 7, cis-3-hexen-1-ol; 8, trans-2 hexenal; 9, decane; 10, limonene; 11, ocimene; 12, undecane; 13, cis-3-hexenyl acetate; 14, methyl salicylate; 15, dodecane; 16, trans-β-farnesene; 17, jasmone; 18, methyl jasmonate; 19, caryophyllene. The 1st-dimensional column was 2.7 m long and was coated with HP-5. The two 2nd-dimensional columns were 0.7 m long and were coated with Carbowax. The 1st-dimensional column was kept at room temperature for 3 min and then heated up to 150 °C at a rate of 20 °C/min. All other components were kept at room temperature. The retention time of a peak is measured at its apex. Curves in (A) are vertically shifted for clarity.

module installed between the 1st- and 2nd-dimensional columns. A mixture of 20 analytes with various volatilities and polarities and plant emitted VOCs were used as model systems and were separated in ~650 s and ~1270 s, respectively. The major advantage of the proposed 2-D GC over the conventional 2-D GC is that it is smarter and more adaptive in analyzing the effluents from the 1st-dimensional column and in selecting the following 2nd-dimensional columns, which can be of various lengths, coatings, flow rates, and temperatures. This unique feature renders the proposed adaptive 2-D GC much higher versatility and significantly enhanced separation capability. It should be emphasized here that the adaptive 2-D GC concept and operation/detection principle presented here are applicable to both 2-D μGC and conventional benchtop 2-D GC systems, regardless of separation columns, detectors, and decision-making modules used in the system.

The use of valves, as reported in our current work, may introduce added dead volumes and cold zones, which potentially results in deteriorated performance. In addition, this type of adaptive GC system relies critically on the first detector to trigger the second dimensional separation and may fail to operate properly when dealing with analytes of extremely low concentrations. A detector with a better sensitivity and a preconcentrator will certainly be needed in the actual system design to mitigate this issue.

Future work will involve use of microfabricated GC columns, microfabricated thermal modulators,[17] integration of on-chip on-column detectors,[37,38] optimization of the flow routing system, and addition of more 2nd-dimensional columns with different lengths and coatings. Faster analysis of vapor analytes in actual applications will also be pursued.

■ ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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