Supplementary Information

Adaptive two-dimensional micro-gas chromatography

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Stop-flow test

Before conducting real 2-D separation, the system was demonstrated to be able to suspend the separation at the 1st-dimensional column without interrupting the separation at the 2^{nd} -dimensional column. The experimental setup was the same as the single 2^{nd} -dimensional column system illustrated in Fig. 2(A), except that the thermal modulator was not in use. The chromatograms shown in Fig. S1(A) were obtained from Detector #1 and #2 with no stop-flow manipulation, which serves as the reference. In the stop-flow test shown in Fig. S1(B), the valve was switched to disconnect the 1st- and 2nd-dimensional column twice. The first time started at t=20 s after the elution of Analyte #1 and the second started at t=180 s after the elution of Analyte #2. The stop-flow (*i.e.*, the disconnection) duration in both cases was 120 seconds. Comparison of the elution times with and without the stop-flow (see details in Table S1) shows that Analyte #2 and #3 in the 1st-dimensional column were delayed once (120 seconds) and twice (240 seconds), respectively, whereas the retention time of all analytes in the 2nd-dimensional column (elution time recorded by Detector #2 – elution time recorded by Detector #1) remained the same. In addition, no significant peak broadening caused by the stop-flow manipulation was observed. These results suggest that, when the 1^{st} - and 2^{nd} -dimensional columns are disconnected, the separation at the 1st-dimensional column can be successfully suspended without any interference to the subsequent separation at the 2nd-dimensional column.

Calculation of retention time at the 1st- and 2nd-dimensional column

The retention time at the 1st- and 2nd-dimensional column can be calculated by the following equations:

1st retention time=Elution time recorded by Detector #1-total prior suspension time in the 1stdimensional column.

 2^{nd} retention time=Elution time recorded by Detector #2–the corresponding thermal modulator turn-on time.

The parameters described in above equations can be found in the real-time chromatogram obtained from Detector #1 and #2. The total prior suspension time in the 1st-dimensional column is represented by the sum of the durations outside the solid boxes that precede the peak recorded by Detector #1. The corresponding thermal modulator turn-on time is represented by the beginning of the dashed box that contains the peak(s) recorded by Detector #2. Below we show some examples.

Single 2nd-dimensional column system. In Fig. 3(A), the 1st retention time of Analyte #2 = 139 s (elution time recorded by Detector #1) – 60 s (total prior suspension time in the 1st-dimensional column) = 79 s. The 2nd retention time of Analyte #2 = 166 s (elution time recorded by Detector #2) – 154 s (the corresponding thermal modulator turn-on time) = 12 s.

Dual 2nd-dimensional column system. In Fig. 5(A), the 1st retention time of Analyte #5 = 52 s (elution time recorded by Detector #1) – 22 s (total prior suspension time in the 1st-dimensional column) = 30 s. The 2nd retention time of Analyte #5 = 64 s (elution time recorded by Detector #2A) – 56 s (the corresponding thermal modulator turn-on time) = 8 s.

Once the 1st- and 2nd-dimensional retention times are known, construction of a 2-D chromatogram becomes very straightforward. The overall 2-D construction process is much simpler than that in a conventional 2-D GC system where tremendous and complex information needs to be extracted and re-assembled.

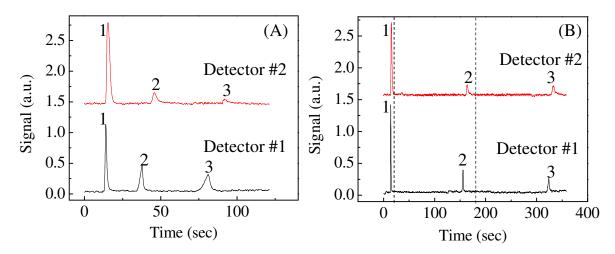


Figure S1. Chromatograms of three alkanes obtained from the adaptive 2-D μ GC system shown in Fig. 2(A), but without using the thermal modulator. (A) Chromatograms corresponding to the configuration in which the 1st- and 2nd-dimensional columns were connected all the time. Curves are vertically shifted for clarity. (B) The 1st- and 2nddimensional columns were disconnected twice. The first disconnection was from 20 s to 140 s (disconnection start-time is marked by the left dashed line and disconnection duration=120 s), and the second from 180 s to 300 s (disconnection start-time is marked by the right dashed line and disconnection duration=120 s). The retention delay of Analyte #2 and #3 in the 1stdimensional (2nd-dimensional) column is 117.7 (117.7) s and 240.8 (240.4) s, respectively. The delay time agrees well with the total disconnection duration that Analyte # 2 and #3 experienced, suggesting that the flow of analytes in the 1st-dimensional column could be completely stopped. Curves are vertically shifted for clarity. Analytes: 1. pentane; 2. octane; 3. nonane. The 1st-dimensional column was 1.5 m long and was coated with RTX-1. The 2nddimensional column was 0.8 m long and was coated with Carbowax.

	Without stop-flow (Fig. S1(A))		With stop-flow (Fig. S1(B))	
	Detector#1	Detector #2	Detector#1	Detector #2
Analyte #1	13.8 s	15.4 s	13.8 s	15.4 s
Analyte #2	37.8 s	46.0 s	155.5 s	163.7 s
			(de1ay=117.7 s)	(de1ay=117.7 s)
Analyte #3	81.2 s	92.2 s	322.0 s	332.6 s
			(de1ay=240.8 s)	(de1ay=240.4 s)

Table S1: Elution times obtained from Fig. S1(A) and (B).