Supplementary material

Manuscript Title: Strategies towards simpler configuration and higher peak capacity with comprehensive multidimensional gas chromatography

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Table S-1. The valve control programs for different heartcut events applied in each comprehensive H/C analysis.

H/C window 5 min No. of experiment = 5÷5 = 1 Run	
Start (min) 8.5	On
13.5	On
18.5	On
23.5	On
28.5	On
33.5	On
38.5	On
43.5	On
End (min) 48.5	On

H/C window 2.5 min No. of experiment = 5÷2.5 = 2 Runs			
Run 1		Run 2	
Start (min) 8.5	On	11	On
11	Off	13.5	Off
13.5	On	16	On
16	Off	18.5	Off
18.5	On	21	On
21	Off	23.5	Off
23.5	On	26	On
26	Off	28.5	Off
28.5	On	31	On
31	Off	33.5	Off
33.5	On	36	On
36	Off	38.5	Off
38.5	On	41	On
41	Off	43.5	Off
43.5	On	46	On
46	Off	48.5	Off
48.5	On	51	On
End (min) 51	Off	53.5	Off

H/C 1.25 min No. of experiment = 5÷1.25 = 4 Runs							
Run 1		Run 2		Run 3		Run 4	
Start (min) 8.5	On	9.75	On	11	On	12.25	On
9.75	Off	11	Off	12.25	Off	13.5	Off
13.5	On	14.75	On	16	On	17.25	On
14.75	Off	16	Off	17.25	Off	18.5	Off
18.5	On	19.75	On	21	On	22.25	On
19.75	Off	21	Off	22.25	Off	23.5	Off
23.5	On	24.75	On	26	On	27.25	On
24.75	Off	26	Off	27.25	Off	28.5	Off
28.5	On	29.75	On	31	On	32.25	On
29.75	Off	31	Off	32.25	Off	33.5	Off
33.5	On	34.75	On	36	On	37.25	On
34.75	Off	36	Off	37.25	Off	38.5	Off
38.5	On	39.75	On	41	On	42.25	On
39.75	Off	41	Off	42.25	Off	43.5	Off
43.5	On	44.75	On	46	On	47.25	On
44.75	Off	46	Off	47.25	Off	48.5	Off
48.5	On	49.75	On	51	On	52.25	On
End (min) 49.75	Off	51	Off	52.25	Off	53.5	Off

H/C 1 min No. of experiment = 5÷1 = 5 Runs									
Run 1		Run 2		Run 3		Run 4		Run 5	
Start (min) 8.5	On	9.5	On	10.5	On	11.5	On	12.5	On
9.5	Off	10.5	Off	11.5	Off	12.5	Off	13.5	Off
13.5	On	14.5	On	15.5	On	16.5	On	17.5	On
14.5	Off	15.5	Off	16.5	Off	17.5	Off	18.5	Off
18.5	On	19.5	On	20.5	On	21.5	On	22.5	On
19.5	Off	20.5	Off	21.5	Off	22.5	Off	23.5	Off
23.5	On	24.5	On	25.5	On	26.5	On	27.5	On
24.5	Off	25.5	Off	26.5	Off	27.5	Off	28.5	Off
28.5	On	29.5	On	30.5	On	31.5	On	32.5	On
29.5	Off	30.5	Off	31.5	Off	32.5	Off	33.5	Off
33.5	On	34.5	On	35.5	On	36.5	On	37.5	On
34.5	Off	35.5	Off	36.5	Off	37.5	Off	38.5	Off
38.5	On	39.5	On	40.5	On	41.5	On	42.5	On
39.5	Off	40.5	Off	41.5	Off	42.5	Off	43.5	Off
43.5	On	44.5	On	45.5	On	46.5	On	47.5	On
44.5	Off	45.5	Off	46.5	Off	47.5	Off	48.5	Off
48.5	On	49.5	On	50.5	On	51.5	On	52.5	On
End (min) 49.5	Off	50.5	Off	51.5	Off	52.5	Off	53.5	Off

H/C 0.5 min

No. of experiment = 5÷0.5 = 10 Runs

Run 1		Run 2		Run 3		Run 4		Run 5		Run 6		Run 7		Run 8		Run 9		Run 10	
Start (min) 8.5	On	9	On	9.5	On	10	On	10.5	On	11	On	11.5	On	12	On	12.5	On	13	On
9	Off	9.5	Off	10	Off	10.5	Off	11	Off	11.5	Off	12	Off	12.5	Off	13	Off	13.5	Off
13.5	On	14	On	14.5	On	15	On	15.5	On	16	On	16.5	On	17	On	17.5	On	18	On
14	Off	14.5	Off	15	Off	15.5	Off	16	Off	16.5	Off	17	Off	17.5	Off	18	Off	18.5	Off
18.5	On	19	On	19.5	On	20	On	20.5	On	21	On	21.5	On	22	On	22.5	On	23	On
19	Off	19.5	Off	20	Off	20.5	Off	21	Off	21.5	Off	22	Off	22.5	Off	23	Off	23.5	Off
23.5	On	24	On	24.5	On	25	On	25.5	On	26	On	26.5	On	27	On	27.5	On	28	On
24	Off	24.5	Off	25	Off	25.5	Off	26	Off	26.5	Off	27	Off	27.5	Off	28	Off	28.5	Off
28.5	On	29	On	29.5	On	30	On	30.5	On	31	On	31.5	On	32	On	32.5	On	33	On
29	Off	29.5	Off	30	Off	30.5	Off	31	Off	31.5	Off	32	Off	32.5	Off	33	Off	33.5	Off
33.5	On	34	On	34.5	On	35	On	35.5	On	36	On	36.5	On	37	On	37.5	On	38	On
34	Off	34.5	Off	35	Off	35.5	Off	36	Off	36.5	Off	37	Off	37.5	Off	38	Off	38.5	Off
38.5	On	39	On	39.5	On	40	On	40.5	On	41	On	41.5	On	42	On	42.5	On	43	On
39	Off	39.5	Off	40	Off	40.5	Off	41	Off	41.5	Off	42	Off	42.5	Off	43	Off	43.5	Off
43.5	On	44	On	44.5	On	45	On	45.5	On	46	On	46.5	On	47	On	47.5	On	48	On
44	Off	44.5	Off	45	Off	45.5	Off	46	Off	46.5	Off	47	Off	47.5	Off	48	Off	48.5	Off
48.5	On	49	On	49.5	On	50	On	50.5	On	51	On	51.5	On	52	On	52.5	On	53	On
End (min) 49	Off	49.5	Off	50	Off	50.5	Off	51	Off	51.5	Off	52	Off	52.5	Off	53	Off	53.5	Off

H/C 0.2 min

No. of experiment = 5÷0.2 = 25 Runs

Run 1		Run 2		Run 3		Run 4		Run 5		Run 6		Run 7		Run 8		Run 9		Run 10		Run 11		Run 12		Run 13	
Start (min) 8.5	On	8.7	On	8.9	On	9.1	On	9.3	On	9.5	On	9.7	On	9.9	On	10.1	On	10.3	On	10.5	On	10.7	On	10.9	On
8.7	Off	8.9	Off	9.1	Off	9.3	Off	9.5	Off	9.7	Off	9.9	Off	10.1	Off	10.3	Off	10.5	Off	10.7	Off	10.9	Off	11.1	Off
13.5	On	13.7	On	13.9	On	14.1	On	14.3	On	14.5	On	14.7	On	14.9	On	15.1	On	15.3	On	15.5	On	15.7	On	15.9	On
13.7	Off	13.9	Off	14.1	Off	14.3	Off	14.5	Off	14.7	Off	14.9	Off	15.1	Off	15.3	Off	15.5	Off	15.7	Off	15.9	Off	16.1	Off
18.5	On	18.7	On	18.9	On	19.1	On	19.3	On	19.5	On	19.7	On	19.9	On	20.1	On	20.3	On	20.5	On	20.7	On	20.9	On
18.7	Off	18.9	Off	19.1	Off	19.3	Off	19.5	Off	19.7	Off	19.9	Off	20.1	Off	20.3	Off	20.5	Off	20.7	Off	20.9	Off	21.1	Off
23.5	On	23.7	On	23.9	On	24.1	On	24.3	On	24.5	On	24.7	On	24.9	On	25.1	On	25.3	On	25.5	On	25.7	On	25.9	On
23.7	Off	23.9	Off	24.1	Off	24.3	Off	24.5	Off	24.7	Off	24.9	Off	25.1	Off	25.3	Off	25.5	Off	25.7	Off	25.9	Off	26.1	Off
28.5	On	28.7	On	28.9	On	29.1	On	29.3	On	29.5	On	29.7	On	29.9	On	30.1	On	30.3	On	30.5	On	30.7	On	30.9	On
28.7	Off	28.9	Off	29.1	Off	29.3	Off	29.5	Off	29.7	Off	29.9	Off	30.1	Off	30.3	Off	30.5	Off	30.7	Off	30.9	Off	31.1	Off
33.5	On	33.7	On	33.9	On	34.1	On	34.3	On	34.5	On	34.7	On	34.9	On	35.1	On	35.3	On	35.5	On	35.7	On	35.9	On
33.7	Off	33.9	Off	34.1	Off	34.3	Off	34.5	Off	34.7	Off	34.9	Off	35.1	Off	35.3	Off	35.5	Off	35.7	Off	35.9	Off	36.1	Off
38.5	On	38.7	On	38.9	On	39.1	On	39.3	On	39.5	On	39.7	On	39.9	On	40.1	On	40.3	On	40.5	On	40.7	On	40.9	On
38.7	Off	38.9	Off	39.1	Off	39.3	Off	39.5	Off	39.7	Off	39.9	Off	40.1	Off	40.3	Off	40.5	Off	40.7	Off	40.9	Off	41.1	Off
43.5	On	43.7	On	43.9	On	44.1	On	44.3	On	44.5	On	44.7	On	44.9	On	45.1	On	45.3	On	45.5	On	45.7	On	45.9	On
43.7	Off	43.9	Off	44.1	Off	44.3	Off	44.5	Off	44.7	Off	44.9	Off	45.1	Off	45.3	Off	45.5	Off	45.7	Off	45.9	Off	46.1	Off
48.5	On	48.7	On	48.9	On	49.1	On	49.3	On	49.5	On	49.7	On	49.9	On	50.1	On	50.3	On	50.5	On	50.7	On	50.9	On
End (min) 48.7	Off	48.9	Off	49.1	Off	49.3	Off	49.5	Off	49.7	Off	49.9	Off	50.1	Off	50.3	Off	50.5	Off	50.7	Off	50.9	Off	51.1	Off

H/C 0.2 min (Continued) **No. of experiment = 5÷0.2 = 25 Run**																							
Run 14		Run 15		Run 16		Run 17		Run 18		Run 19		Run 20		Run 21		Run 22		Run 23		Run 24		Run 25	
Start (min) 11.1	On	11.3	On	11.5	On	11.7	On	11.9	On	12.1	On	12.3	On	12.5	On	12.7	On	12.9	On	13.1	On	13.3	On
11.3	Off	11.5	Off	11.7	Off	11.9	Off	12.1	Off	12.3	Off	12.5	Off	12.7	Off	12.9	Off	13.1	Off	13.3	Off	13.5	Off
16.1	On	16.3	On	16.5	On	16.7	On	16.9	On	17.1	On	17.3	On	17.5	On	17.7	On	17.9	On	18.1	On	18.3	On
16.3	Off	16.5	Off	16.7	Off	16.9	Off	17.1	Off	17.3	Off	17.5	Off	17.7	Off	17.9	Off	18.1	Off	18.3	Off	18.5	Off
21.1	On	21.3	On	21.5	On	21.7	On	21.9	On	22.1	On	22.3	On	22.5	On	22.7	On	22.9	On	23.1	On	23.3	On
21.3	Off	21.5	Off	21.7	Off	21.9	Off	22.1	Off	22.3	Off	22.5	Off	22.7	Off	22.9	Off	23.1	Off	23.3	Off	23.5	Off
26.1	On	26.3	On	26.5	On	26.7	On	26.9	On	27.1	On	27.3	On	27.5	On	27.7	On	27.9	On	28.1	On	28.3	On
26.3	Off	26.5	Off	26.7	Off	26.9	Off	27.1	Off	27.3	Off	27.5	Off	27.7	Off	27.9	Off	28.1	Off	28.3	Off	28.5	Off
31.1	On	31.3	On	31.5	On	31.7	On	31.9	On	32.1	On	32.3	On	32.5	On	32.7	On	32.9	On	33.1	On	33.3	On
31.3	Off	31.5	Off	31.7	Off	31.9	Off	32.1	Off	32.3	Off	32.5	Off	32.7	Off	32.9	Off	33.1	Off	33.3	Off	33.5	Off
36.1	On	36.3	On	36.5	On	36.7	On	36.9	On	37.1	On	37.3	On	37.5	On	37.7	On	37.9	On	38.1	On	38.3	On
36.3	Off	36.5	Off	36.7	Off	36.9	Off	37.1	Off	37.3	Off	37.5	Off	37.7	Off	37.9	Off	38.1	Off	38.3	Off	38.5	Off
41.1	On	41.3	On	41.5	On	41.7	On	41.9	On	42.1	On	42.3	On	42.5	On	42.7	On	42.9	On	43.1	On	43.3	On
41.3	Off	41.5	Off	41.7	Off	41.9	Off	42.1	Off	42.3	Off	42.5	Off	42.7	Off	42.9	Off	43.1	Off	43.3	Off	43.5	Off
46.1	On	46.3	On	46.5	On	46.7	On	46.9	On	47.1	On	47.3	On	47.5	On	47.7	On	47.9	On	48.1	On	48.3	On
46.3	Off	46.5	Off	46.7	Off	46.9	Off	47.1	Off	47.3	Off	47.5	Off	47.7	Off	47.9	Off	48.1	Off	48.3	Off	48.5	Off
51.1	On	51.3	On	51.5	On	51.7	On	51.9	On	52.1	On	52.3	On	52.5	On	52.7	On	52.9	On	53.1	On	53.3	On
End (min) 51.3	Off	51.5	Off	51.7	Off	51.9	Off	52.1	Off	52.3	Off	52.5	Off	52.7	Off	52.9	Off	53.1	Off	53.3	Off	53.5	Off

Investigation of experimental conditions in GC×GC

GC×GC employed long ^{1}D column (30 m) and short ^{2}D column (5 m) enabling fast ^{2}D separation of technical glycol precursor sample (with compounds elution time mostly distributing within a window of 6 s). As a result, comprehensive analysis was performed within a single run (a single injection). Flow modulator was applied in this approach which requires high ^{2}D flow for effective modulation process [15, 16]. The outlet flow was thus split to decrease flow to MS by using DS as a splitter [17] as shown in **Fig. 1A**. The flow was further reduced by use of a longer restrictor with the same I.D. to MS.

Effects of injection time and ^{2}D column flow

With a constant ^{1}D flow of 0.8 mL/min, different injection times and ^{2}D column flows were investigated in this study. The corresponding GC×GC results were evaluated according to n_c (related to average peak width), total peak area (indicating greater peak focusing effect during the modulation) and the number of identified compounds as shown in **Fig. S1**. Change of modulator injection time and ^{2}D flow in GC×GC significantly affected $^{2}w_{b,ave}$ and total intensity (see ^{2}D width at blob base and total volume data in **Fig. S1A** and **S1B**); whilst, $^{1}w_{b,ave}$ slightly varied as shown by similar ^{1}D width at blob base values plotted in **Fig. S1C**.

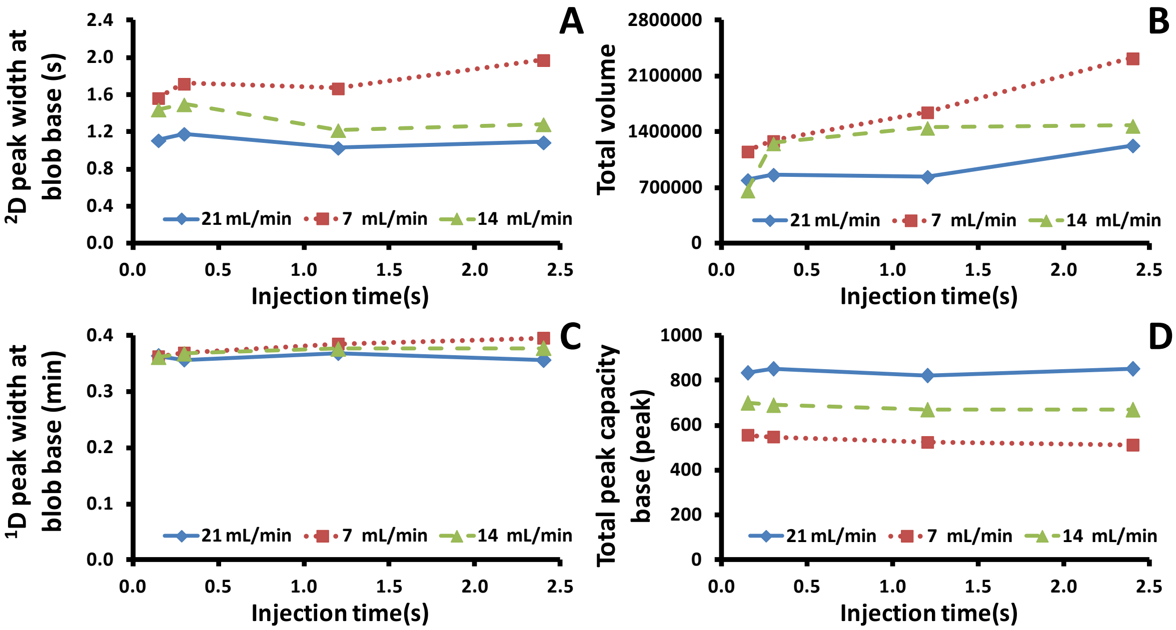

Fig. **S1.** Effects of modulator injection time on separation performance using different ^{2}D column flows: 21, 14 and 7 mL min^{-1} (♦, Δ and □, respectively).

With a constant ^{2}D flow of 21 mL min^{-1}, different modulator injection time was applied with the results shown in **Fig. S2**. Injection time is a period in which a pulse from the end of ^{1}D column is filled into the channel inside the modulator prior to injection onto ^{2}D column. This is a critical parameter in GC×GC which could cause peak dispersion or breakthrough during the modulation process. With the studied conditions, too short injection time (0.15 s) could cause peak fronting as shown by the downward plateau of the peaks located between 20-30 min $^{1}t_R$ in **Fig. S2**; whilst, too long injection time (2.40 s) led to peak tailing (*e.g.* see the upward plateau of the peaks located between 20-30 min $^{1}t_R$ in **Fig. S2**). An effective injection time was selected to be 0.60 s reducing effects of peak broadening as shown by the minimum ^{2}D width at blob base ($^{2}w_{b,ave}$) with the 2D flows of 21 and 14 mL min^{-1} in **Fig. S1A**

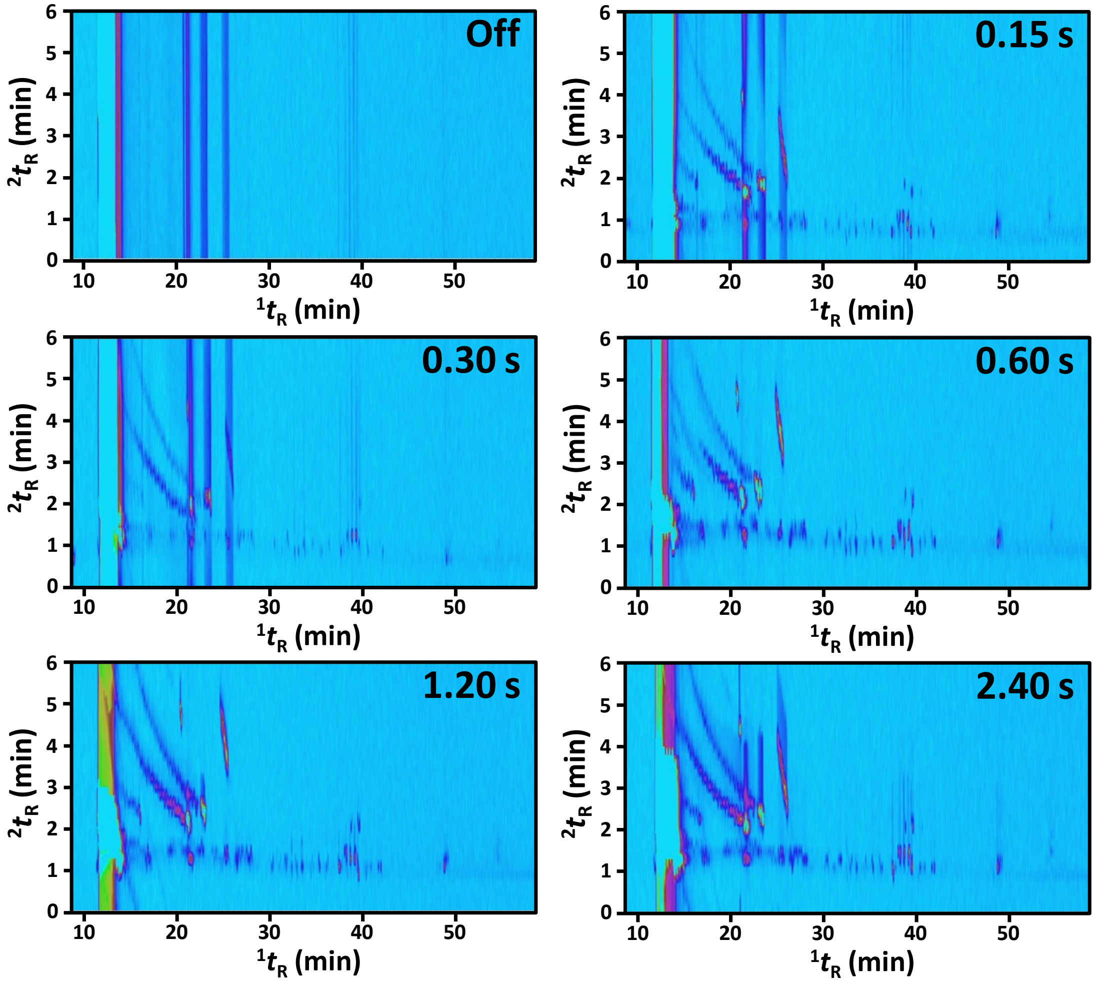

Fig. S2. GC×GC results obtained by using different injection time (0.15-2.40 s) using a constant ^{1}D and ^{2}D column flows of 0.8 and 21 mL min^{-1}, respectively.

It should be noted that a suitable condition cannot be only that resulting in the best performance, *e.g.* with the highest n_c at 21 mL min^{-1} of ^{2}D flow and 0.60 s injection time (**Fig. S1D**) or highest total volume (total intensity) at 7 mL min^{-1} of ^{2}D flow and 0.60 s injection time (**Fig. S1D**). Other factors need to be taken into account. Use of high pressure at the modulator is required for effective modulation process (*e.g.* well focused peaks or prevention of leakage), which resulted in high ^{2}D flow. However, low flow is required to preserve lifetime of MS vacuum pump and improved sensitivity, as well as providing effective flow of 20-40 cm s^{-1} with He as carrier gas. The ^{2}D flow should thus be decreased. However, too low ^{2}D flow also causes ineffective modulation process, *e.g.* further resulting in weak focussing effect or peak splitting, and peak broadening. With a constant injection time of 0.6 s, different ^{2}D flow was applied with the results shown in **Fig. S3**.

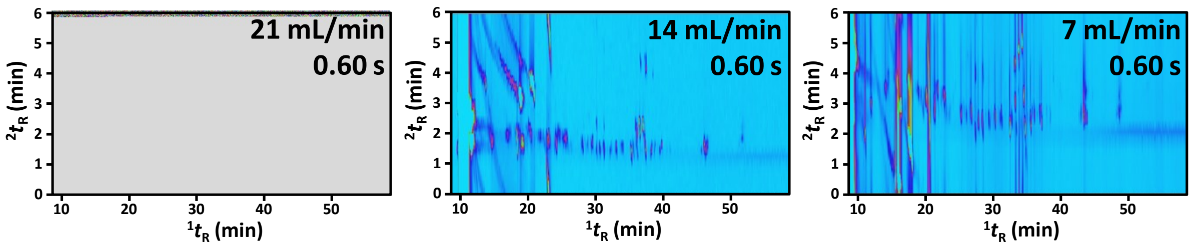

Fig. S3. GC×GC results obtained by using different ^{2}D column flow (21, 14 and 7 mL min^{-1}) using a constant ^{1}D column flow and injection time of 0.8 mL min^{-1} and 0.60 s, respectively.

The result showed improved separation (also with broader peaks) at lower flow due to the increasing void time. However, modulation performance decreased at the lower ^{2}D column flow as can be seen with the significantly broader peak width in ^{2}D separation, see the larger ^{2}D width at blob base ($^2w_{b,ave}$) by using ^{2}D flow of 7 mL min^{-1} in **Fig. S1A**, as well as the split peaks (*e.g.* that after 40 min) by this flow in **Fig. S1**. Based on the improved separation performance with significantly high intensity and low ^{2}D flow, 14 mL min^{-1} of ^{2}D flow and 0.60 s of injection time were selected for further analysis with compound identification.

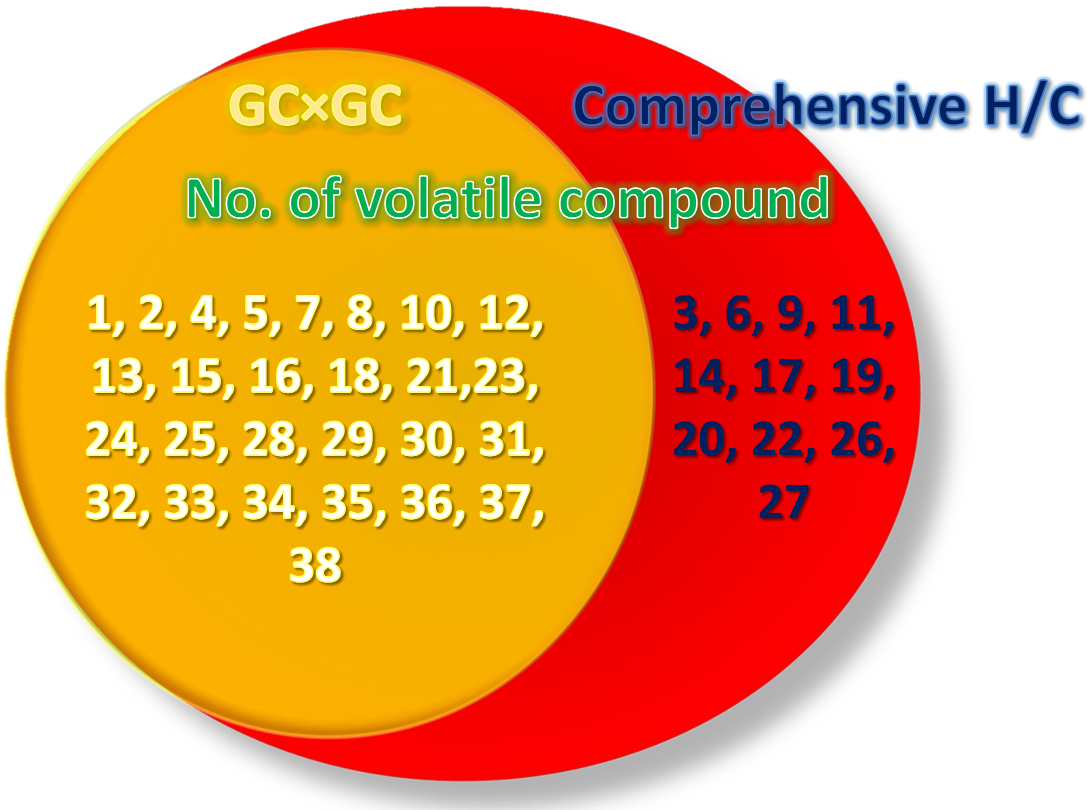

Fig. S4. Venn diagram showing the number of identified compounds in **Table 1** using GC×GC and the comprehensive H/C MDGC techniques.