DIRECT FLOW MODULATION METHOD FOR COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY

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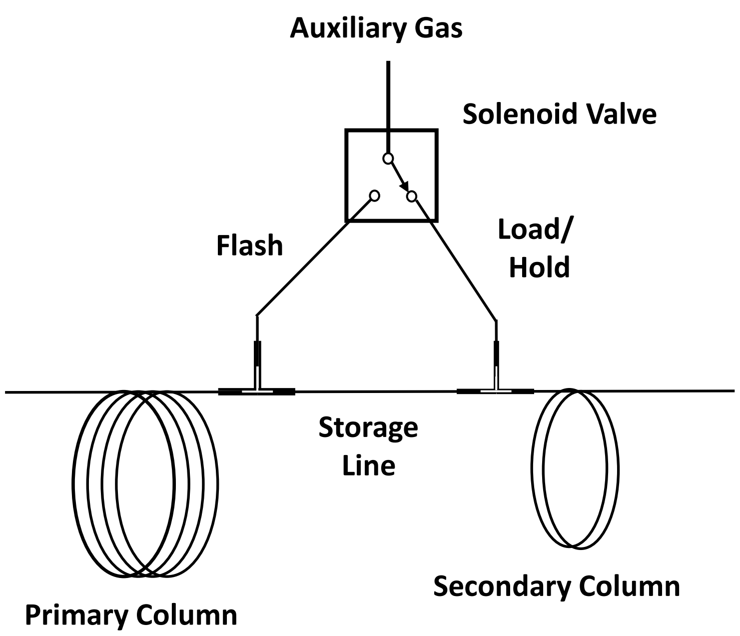
INTRODUCTION

- There are two kinds of GC x GC modulators
  - Thermal modulator
  - Valve/Flow modulator
- The thermal modulation method has the advantages of good performance (makes sharp secondary peaks) and concentrates primary simultaneously. However, its costs are high and not good for low boil compounds
- The valve/flow modulator has the advantages of simple, low cost, and good for low boil compounds
- The flow modulation can be classified as
  - Switch flow modulation
  - Direct flow modulation
- This presentation will discuss the direct flow modulation method.

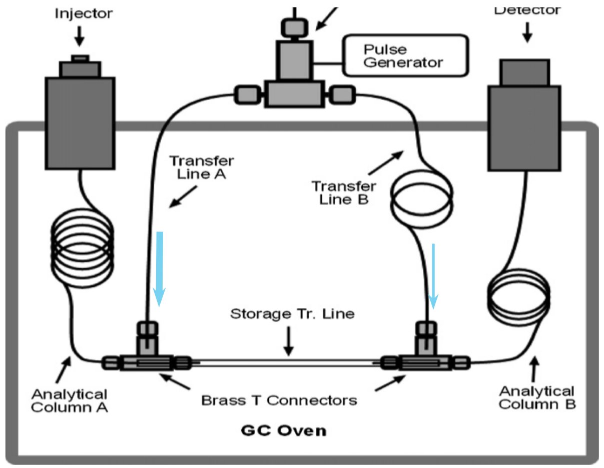
SWITCH FLOW MODULATION METHOD REVIEW

TYPICAL FLOW MODULATION



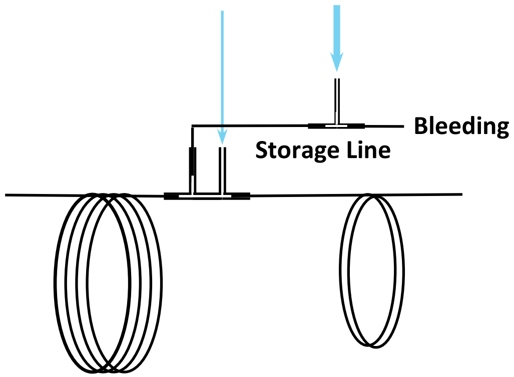
First proposed: Flow-switching device for comprehensive two-dimensional gas chromatography
Pedro A. Bueno Jr., John V. Seeley*
Journal of Chromatography A, 1027 (2004) 3-10

PULSE FLOW MODULATION



Pulsed flow modulation comprehensive two-dimensional gas chromatography
Marina Poliak, Maya Kochman, Aviv Amirav*
Journal of Chromatography A, 1186 (2008) 189-195

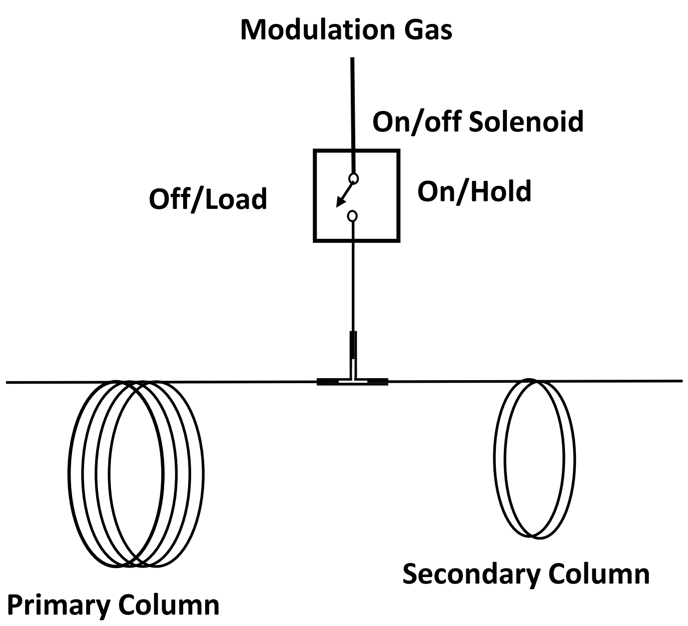
REVERSE FLOW MODULATION



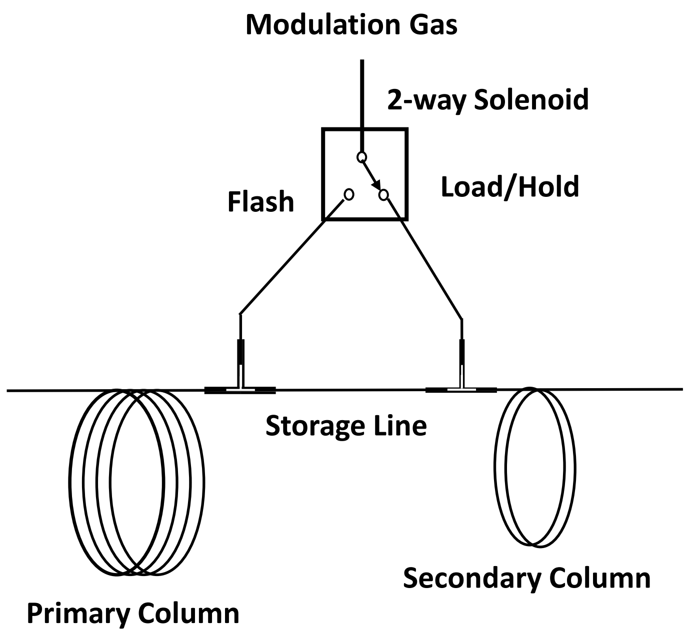
A reversed-flow differential flow modulator for comprehensive two-dimensional gas chromatography
James F. Griffith, William L. Winniford, Kefu Sun, Rob Edam, Jim C. Luong*
Journal of Chromatography A, 1226 (2012) 116-123

DIRECT FLOW MODULATION AND COMPARE WITH SWITCH MODULATION

DIRECT FLOW MODULATION



SWITCH FLOW MODULATION

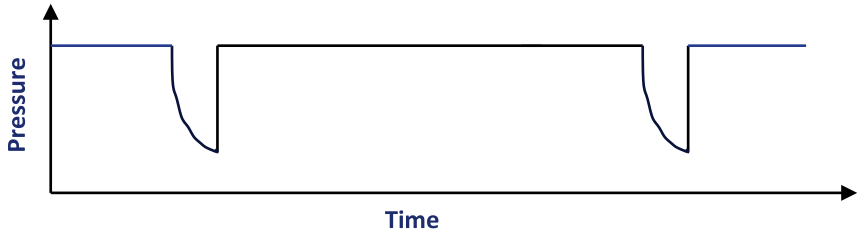


DIFFERENCES

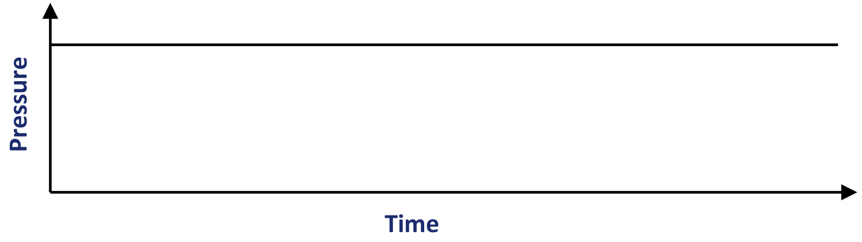
- Only one T connected between primary and secondary column and no storage line.
- On/off solenoid volve instead of 2-way solenoid valve.
- Way to modulation and deriver primary sample
- Pressure at the primary and secondary join.

PRESSURE CHANGE DIFFERENCE AND DIRECT FLOW MODULATION PROCESS

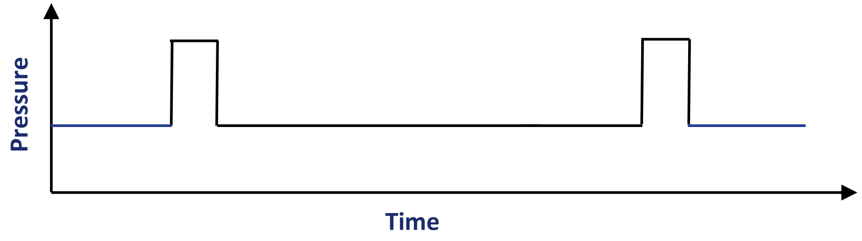
DIRECT FLOW MODULATION



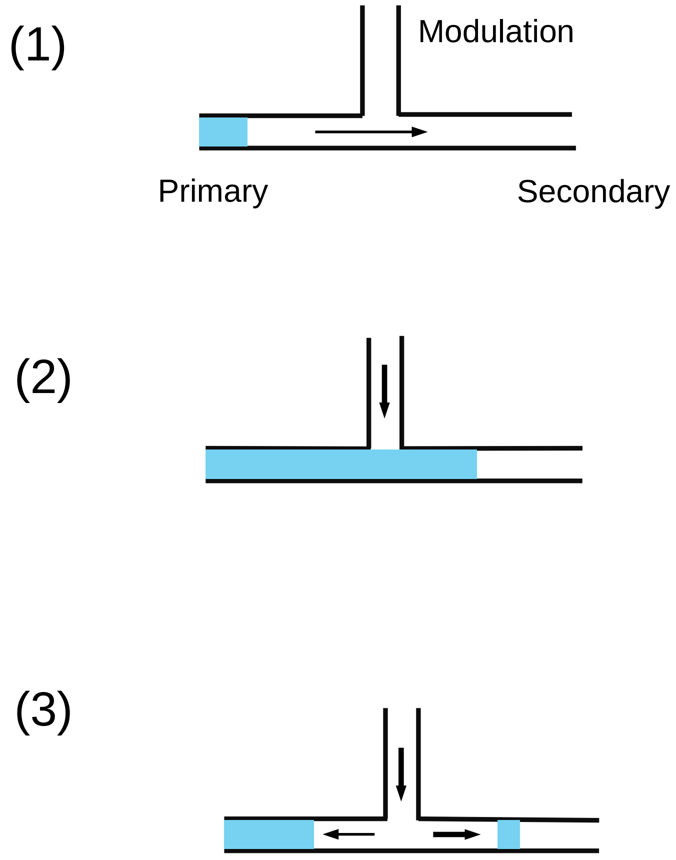
SWITCH FLOW MODULATION



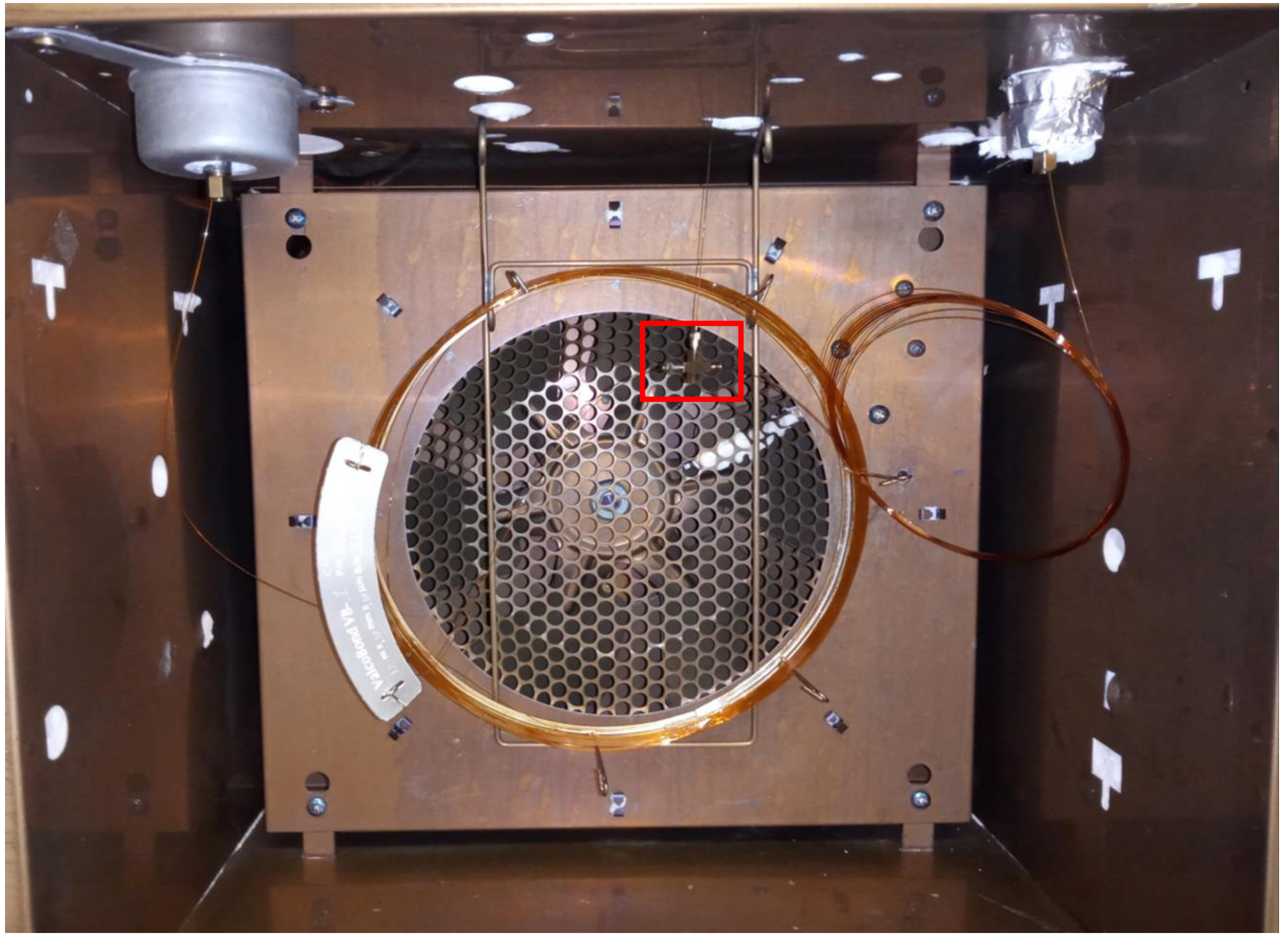
PULSE FLOW MODULATION



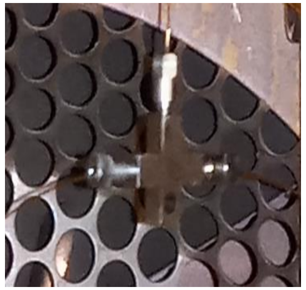
DIRECT FLOW MODULATION PROCESS

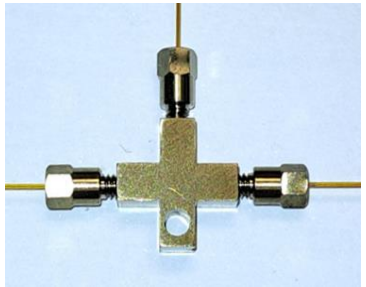


EXPERIMENTAL SETUP



360 Tee

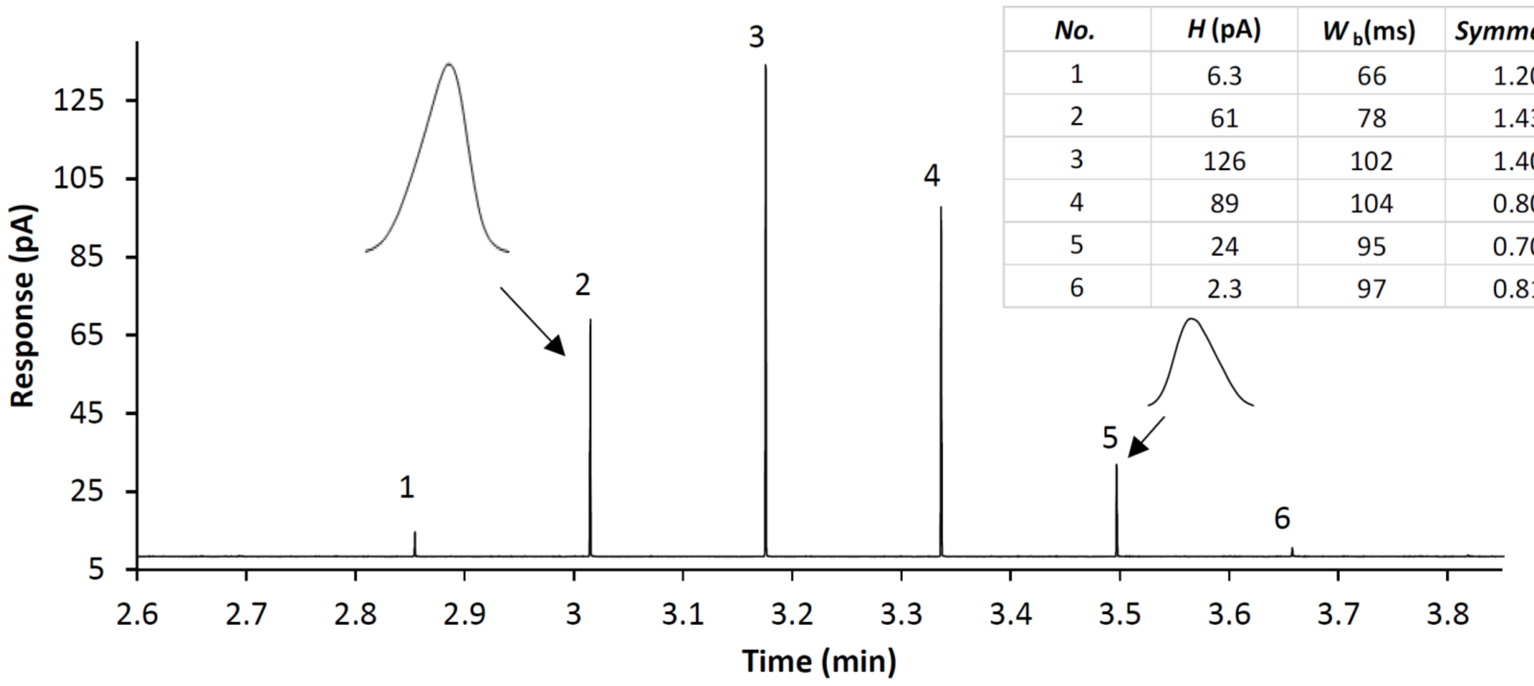




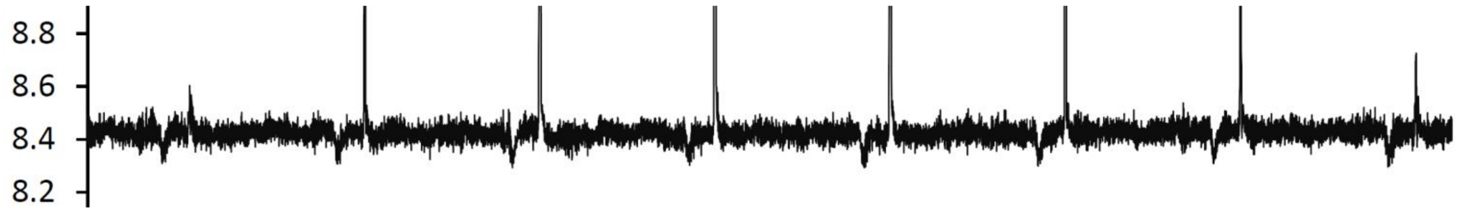
ADVANTAGES:

- Small internal and dead volume
- Less mass, no extra heat needed
- Can withstand high temperature
- Long lifetime

TYPICAL MODULATED CH_4 PEEK BY DIRECT FLOW MODULATION METHOD



No.	*H* (pA)	W_b(ms)	*Symmetry*
1	6.3	66	1.20
2	61	78	1.43
3	126	102	1.40
4	89	104	0.80
5	24	95	0.70
6	2.3	97	0.81



Primary column:
VB-1 30m×0.25mm×1.0µm

Secondary column:
VB-1 5m×0.25mm×0.25µm

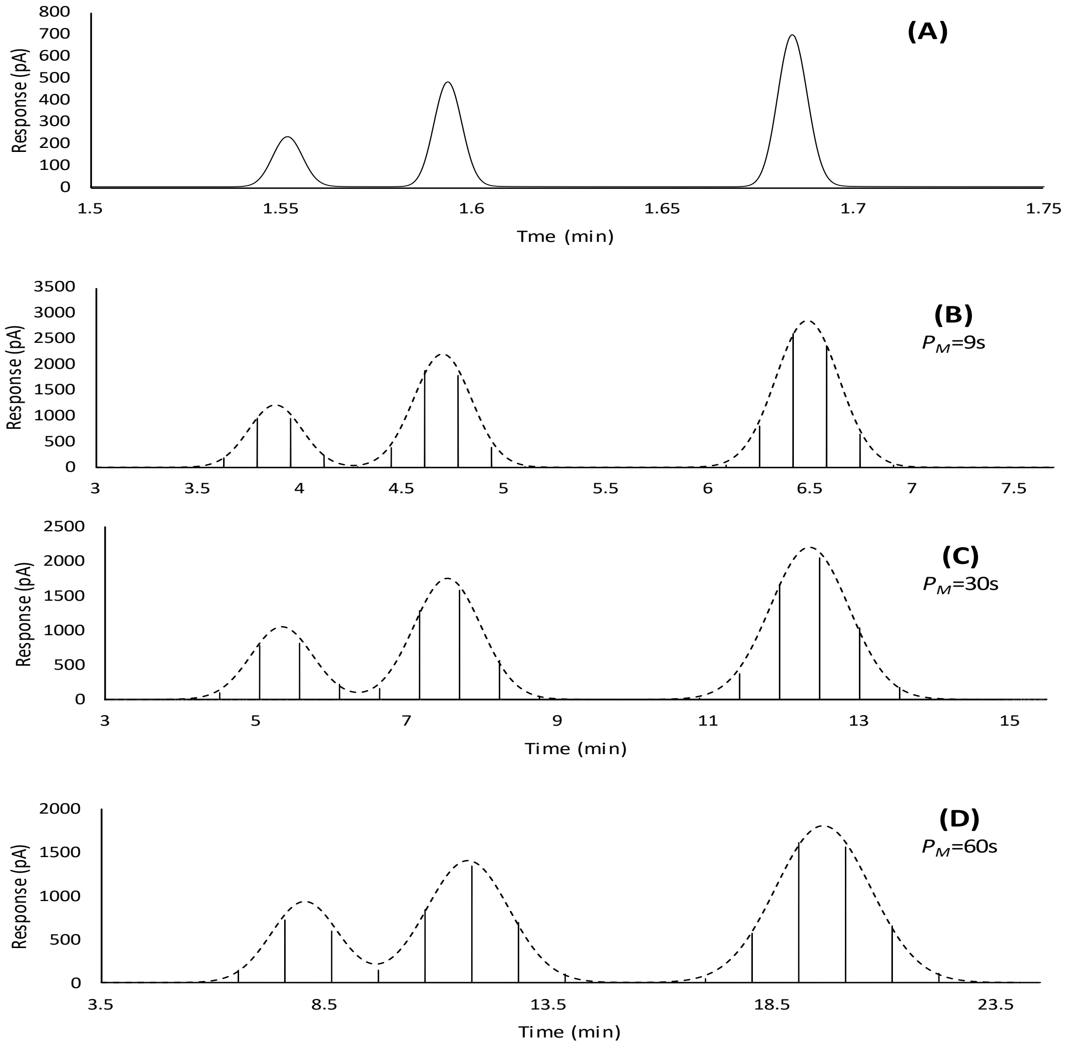
Oven temperature: 50 ºC

Sample: 100ppm CH_4, 2µL

The static column flow rates at FID end: 2.60 mL/min when the valve is in OFF/LOAD position. 20.0 mL/min in On/HOLD position.

Loading time: 0.2 s
Modulation period: 10 s

C_1 TO C_3 PRIMARY SEPARATION

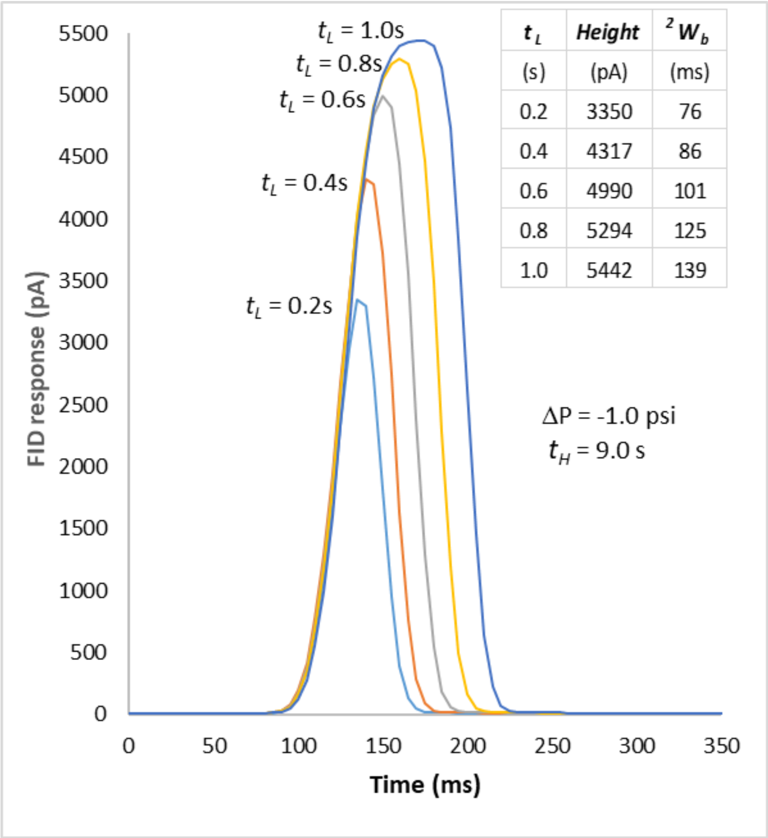


P_M	T_R (CH4)	$W_{1/2}$ (CH4)	H (CH4)	SN(C2/C3)
(s)	(min)	(min)	(pA)	
1D	1.55	0.0094	226	1.5
9	3.88	0.186	1210	1.1
30	5.34	0.58	1050	0.8
60	8.05	1.06	930	0.4

VICI

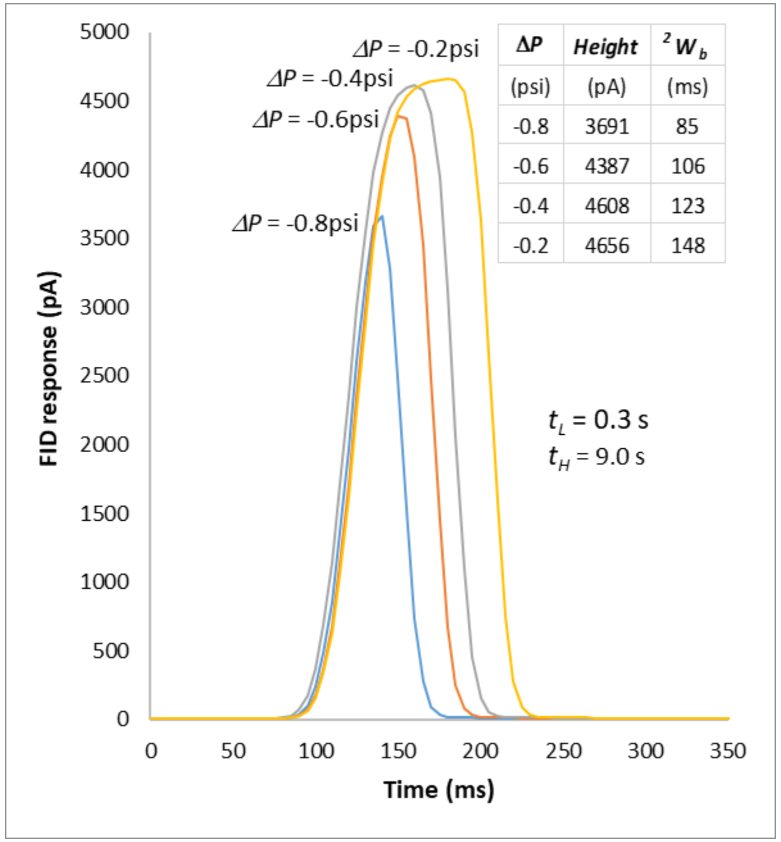
SECONDARY DIMENSION PEAK PROFILE

LOADING TIME T_L



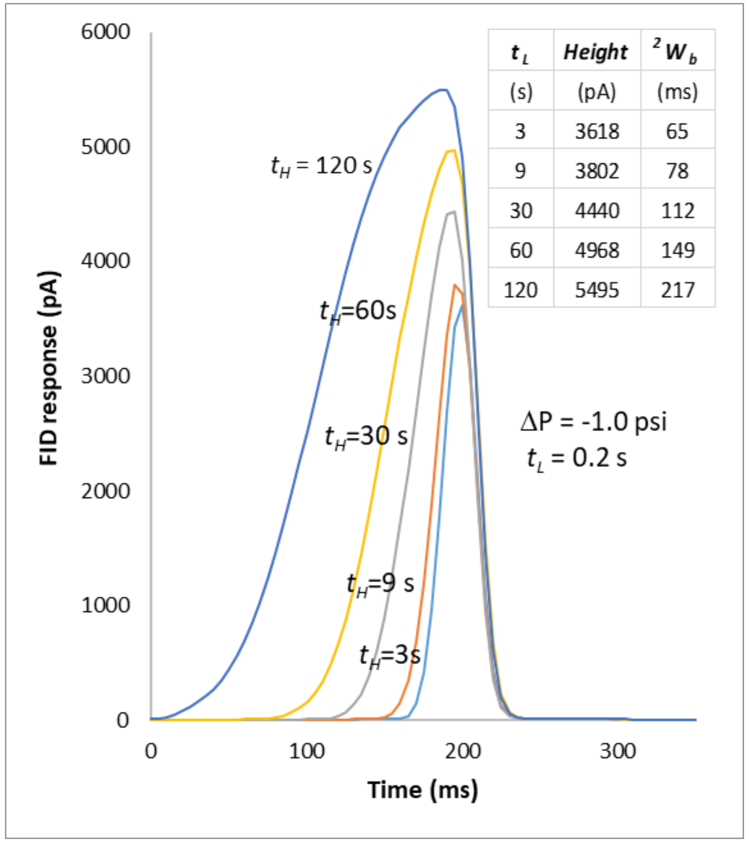
t_L (s)	Height (pA)	^2W_b (ms)
0.2	3350	76
0.4	4317	86
0.6	4990	101
0.8	5294	125
1.0	5442	139

PRESSURE DIFFERENCE ΔP



ΔP (psi)	Height (pA)	^2W_b (ms)
-0.8	3691	85
-0.6	4387	106
-0.4	4608	123
-0.2	4656	148

HOLDING TIME T_H



t_L (s)	Height (pA)	^2W_b (ms)
3	3618	65
9	3802	78
30	4440	112
60	4968	149
120	5495	217

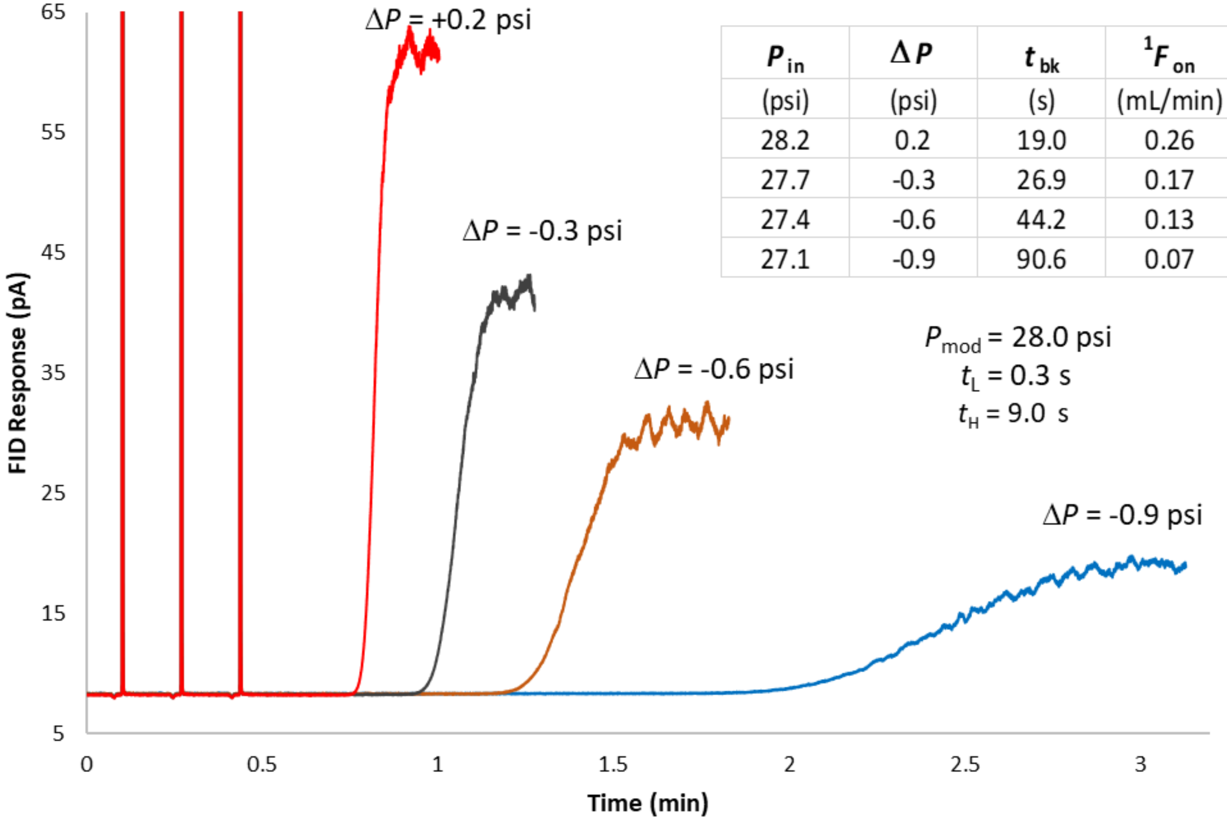
t_L = loading time.
t_H = Holding time.
ΔP = Pressure difference between inlet and modulation point $= P_{in} - P_{mod}$

SIGNAL ENHANCEMENT AND REPEATABILITY

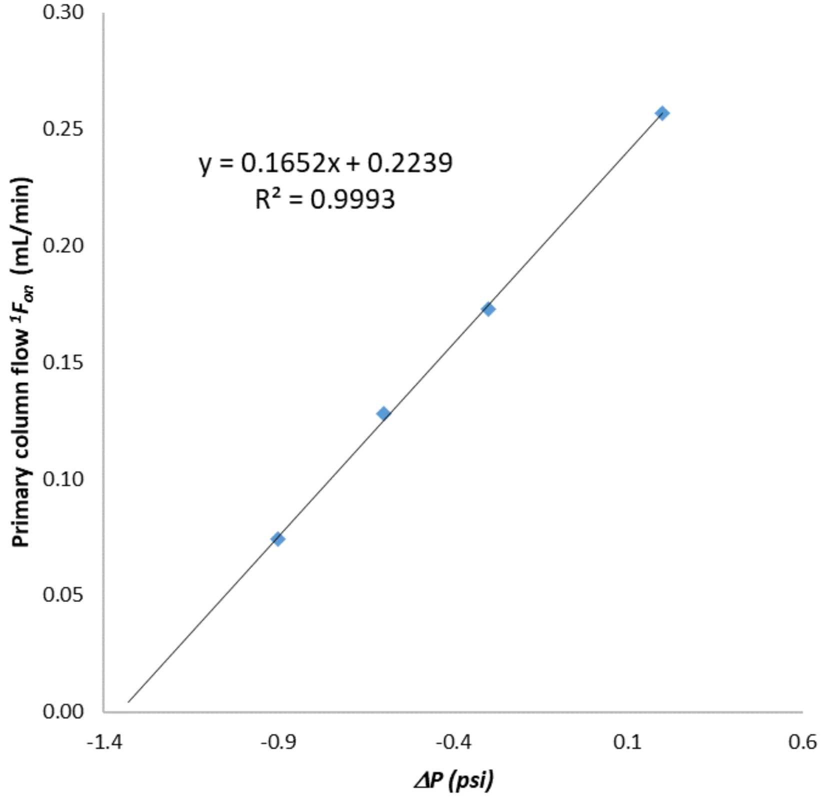
t_L	P_{in}	Secondary peak height (pA)					Pri. CH_4 level	Signal ratio
(s)	(psi)	Run1	Run2	Run3	Avg.	RSD(%)	(pA)	
0.3	27.0	3666	3644	3646	3652	0.33	620	5.89
	27.4	4538	4538	4541	4539	0.03	620	7.32
	27.8	4419	4432	4433	4428	0.17	620	7.14
	28.2	4278	4288	4292	4286	0.17	620	6.91
0.6	27.1	4776	4802	4804	4794	0.32	625	7.67
	27.4	4763	4772	4783	4772	0.21	625	7.64
	27.7	4763	4772	4783	4772	0.21	625	7.64
	28.2	4553	4587	4573	4571	0.37	625	7.31

t_H = 9.0 s
P_{mod} = 28.0 psi

PRESSURE DIFFERENCE ΔP TO THE BREAKTHROUGH TIME

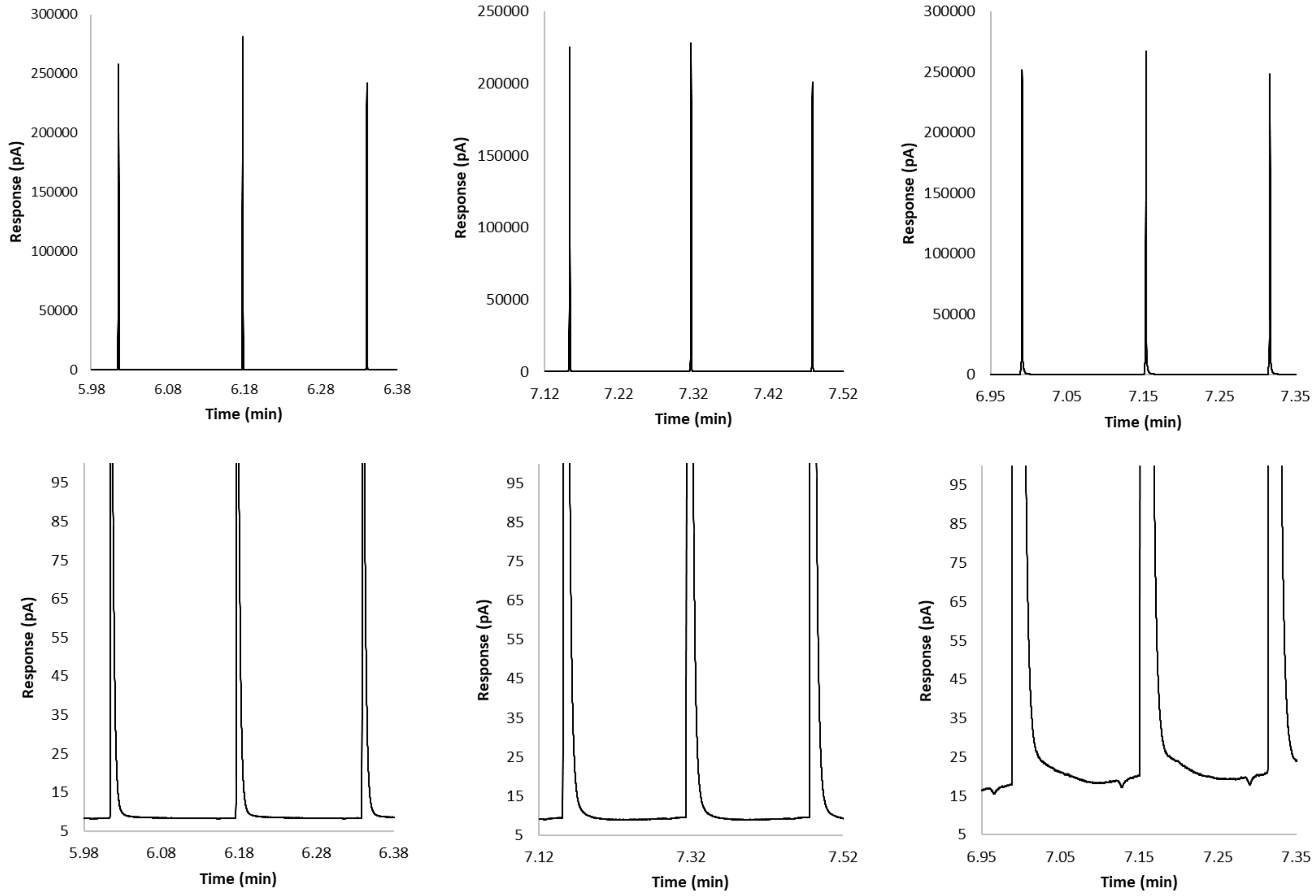


P_{in} (psi)	ΔP (psi)	t_{bk} (s)	${}^1F_{on}$ (mL/min)
28.2	0.2	19.0	0.26
27.7	-0.3	26.9	0.17
27.4	-0.6	44.2	0.13
27.1	-0.9	90.6	0.07



N-PENTANE SOLVENT MODULATION

360 T | 1/32” T | 1/16” T



Tee	$W_{1/2}$ (ms)	W_b (ms)
360	63.4	860
1/32	63.6	1,585
1/16	69.4	2,445

Primary column:
VB-1 30m×0.25mm×1.0μm

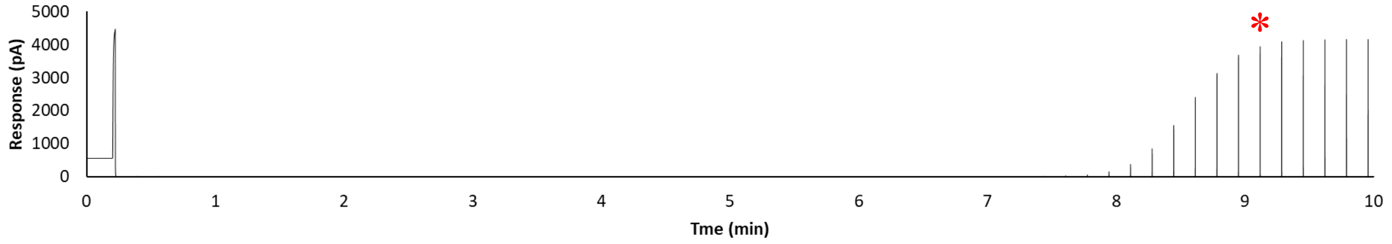
Secondary column:
VB-1 5m×0.25mm×0.25μm

Oven temperature: 50 ^{o}C

Sample: 1 μL Pentane, 100:1

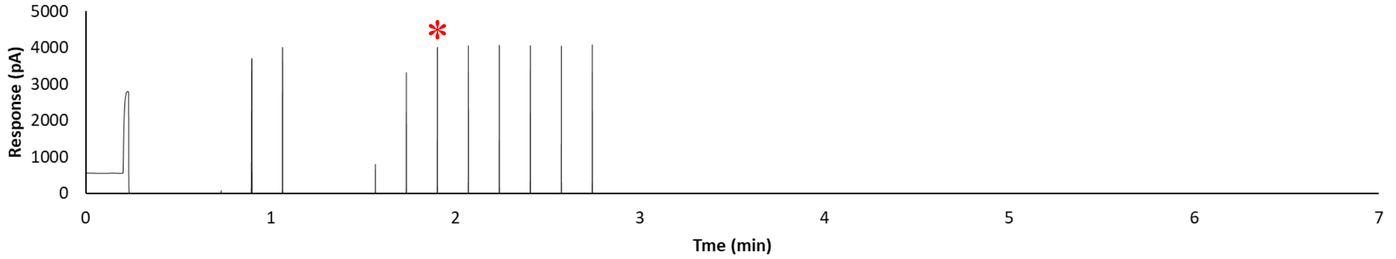
Loading time: 0.2 s
Modulation period: 10 s

WAIT TIME FROM 1D TO GC×GC



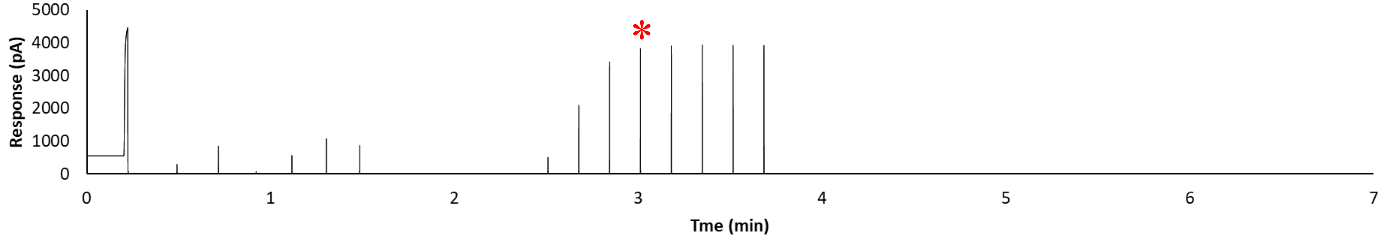
Normal start

* 9.28 min, 54 cycles.



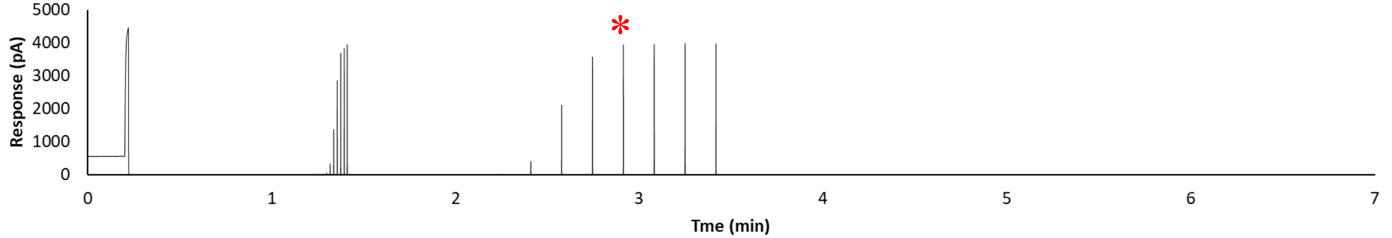
Program modulation pressure from 20 psi to 28 psi at 8.0 psi/min

* 1.90 min, 10 cycles.



Program loading time, start with t_L = 6.4, 3.9, 2.7, 2.1, 1.7, 1.4, 1.1, 0.9, 0.7, 0.6 s

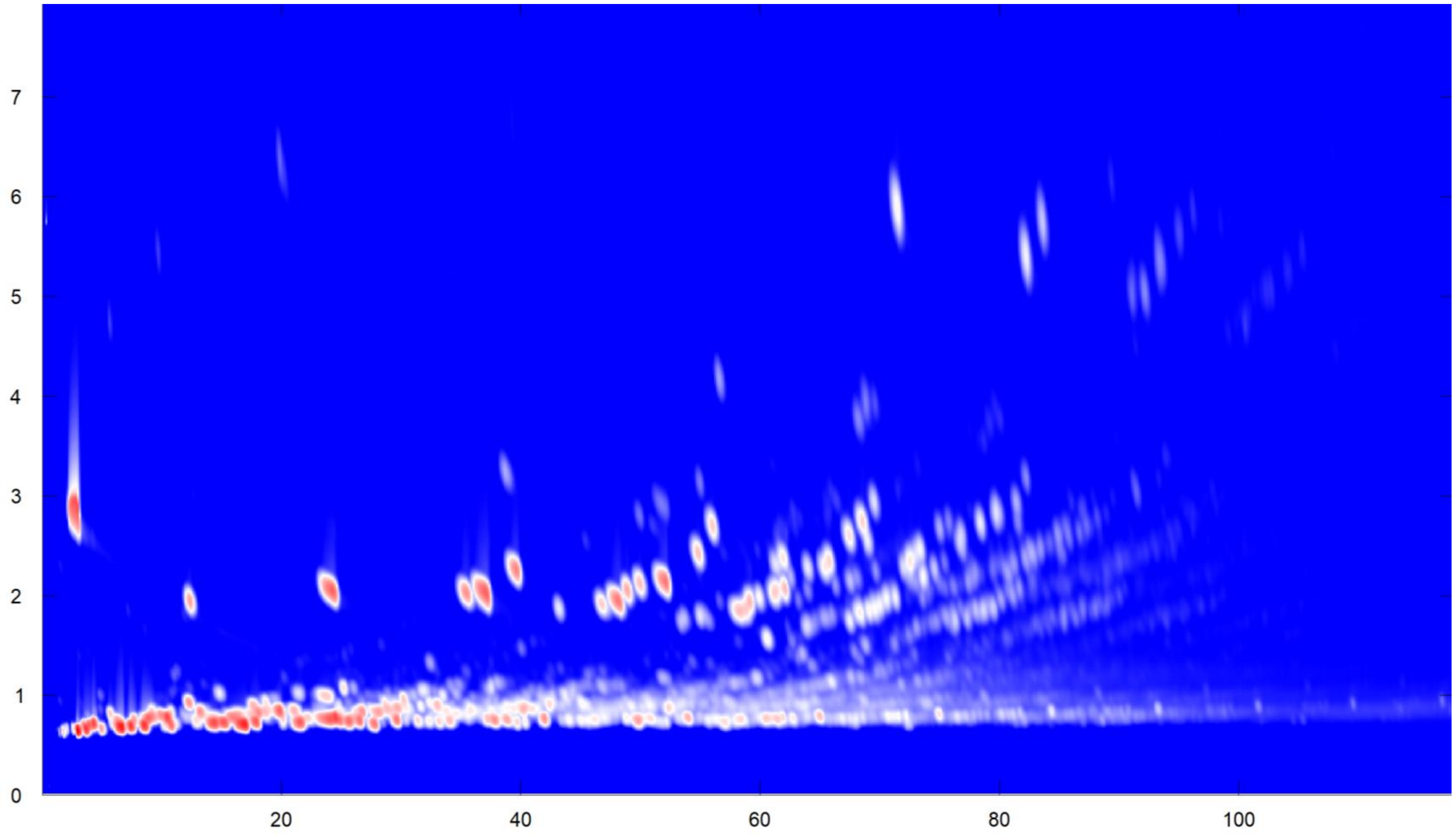
* 3.01 min, 16 cycles.



High frequency at beginning -63 fast cycles and 9 normal cycles

* 2.91 min, 63+9 cycles.

A GASOLINE SAMPLE



Primary: HP-1
15m × 0.25mm × 0.25µm

Secondary: VB-wax
5m × 0.25mm × 0.25µm

Oven: 35 °C (1 min) to 220 °C at 1.4 °C/min

Secondary Flow: 20 mL/min constant flow mode

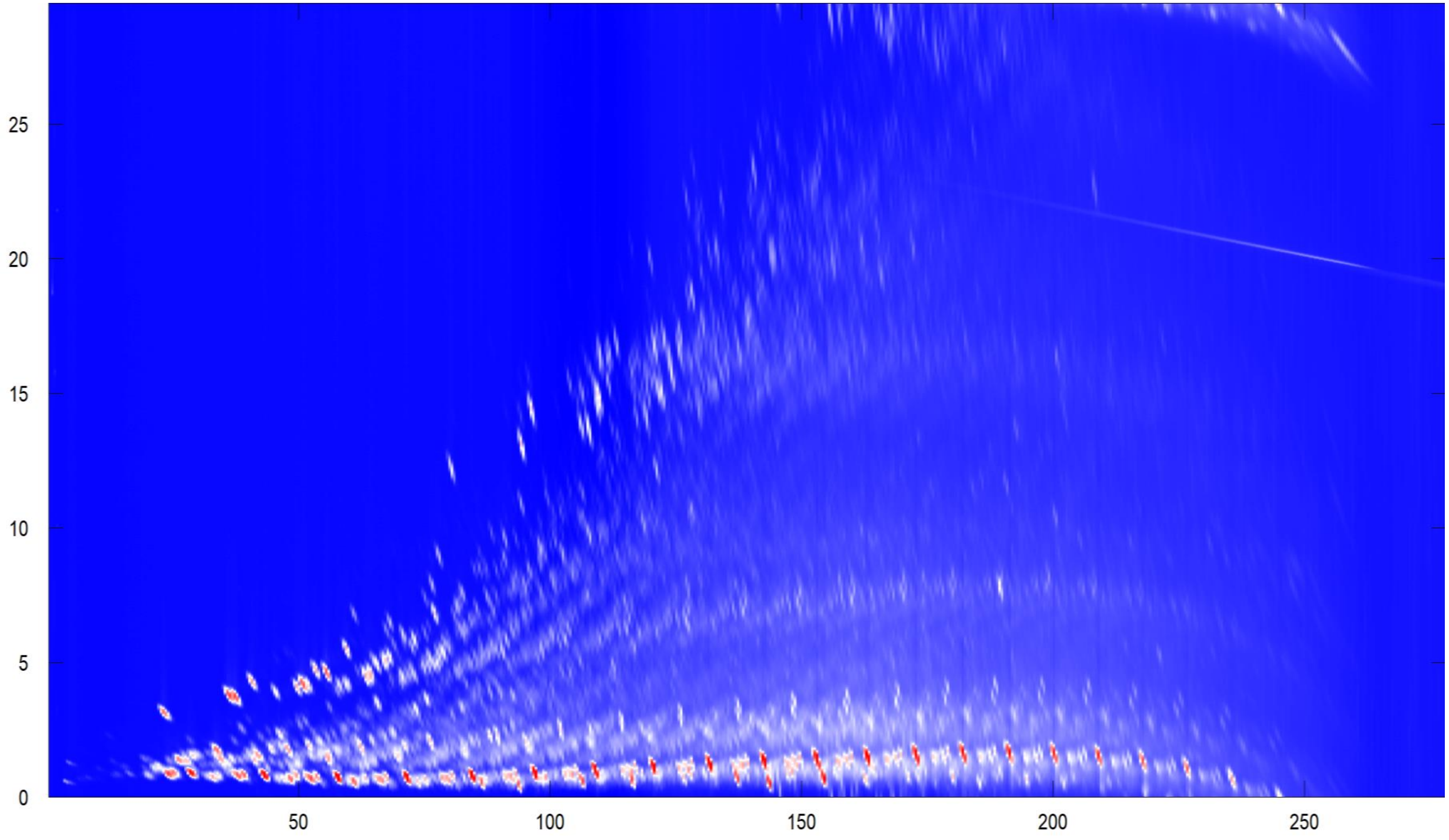
Pressure at Inlet: Programed from 26.2 psi to 44.7 psi at 0.14 psi/min

Loading Time: 0.6 s

Holding Time: 7.2 s

P_M : 7.8 s

REFERENCE GAS OIL (RGO)



Primary Column: VB-1, 12m×0.10mm×0.10µm

Secondary Column: HP-17ms, 10mx0.18mm×0.18µm

Oven Temperature: 70 °C to 320 °C at 0.90 °C/min

Secondary Flow: 5.0 mL/min constant flow mode

Inlet Pressure: Programed from 48.3 psi to 91.6 psi at 0.14 psi/min

Loading Time: 1.1 s

Holding Time: 27.0 s

P_M: 28.1 s

CONCLUSIONS

- The direct flow modulation is a simple, robust, and low-cost modulation method for GCxGC.
- It can achieve less than100 ms $^{2}W_{b}$ and as long as 120 s secondary time range with 100% transfer from primary to secondary dimension.
- Since the solenoid valve is mounted outside the GC oven and 360 fittings are used, this modulator can work at temperatures up to the column temperature limit.
- However, it is sensitive to pressure and flowrate change and require longer time to switch from 1D to GC x GC.

THANK YOU