SAND2013-3841C

A Portable Microfabricated GCxGC System for Vapor Sampling and Analysis

37th International Symposium on Capillary Chromatography
and
10th GCxGC Symposium
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3 Degrees of Separation
Advanced Analytical Technologies

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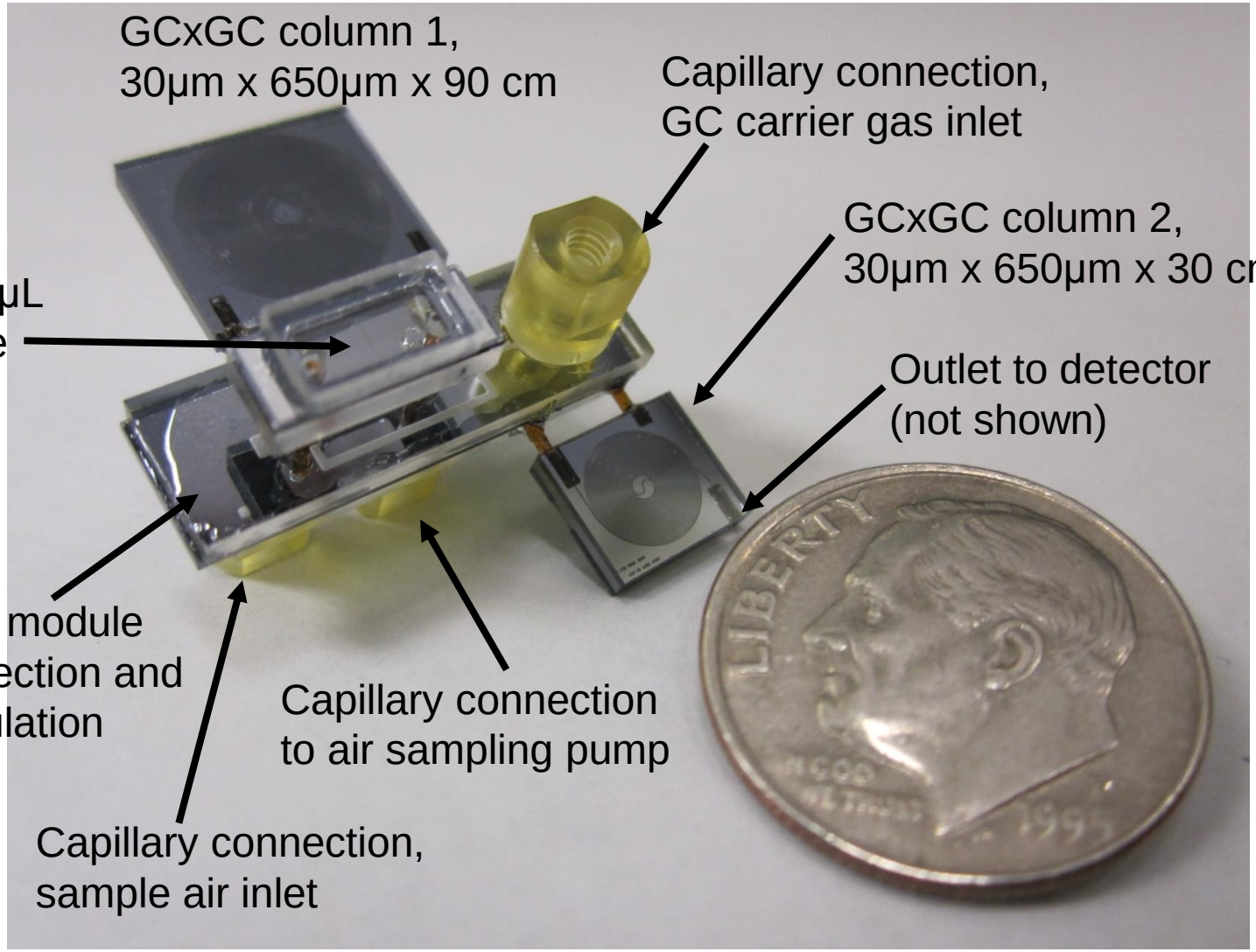
Previously Reported Design:
We have built and tested 8 of these



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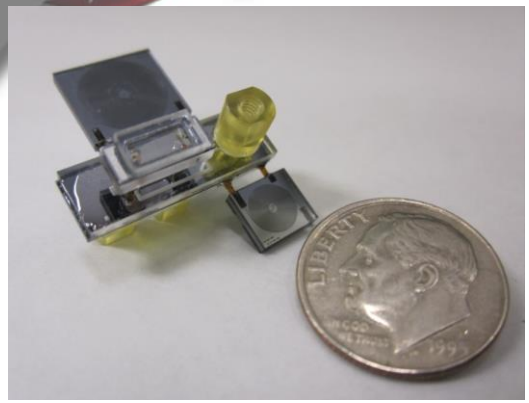
Design Changes Now Ongoing



← Why did the first design look like this?

- ***SPEED*** – 4 second analysis cycle: Air sampling, GCxGC separation, detection, data analysis and alarm reporting
- Sensitivity – 1 ppt limit of detection requires fast sample injection (*splitless!)*
- Low power, small volume

Current design changes driven by:

1. Performance problems with the above design
   - GCxGC modulation flow restriction at junction between GC1 and GC2
   - Low device yield and robustness of sampling microvalve arrays
   - Sample injection speed limitations

2. Customer-requested changes
   - Ambient air carrier gas
   - Vacuum outlet GC (for compatibility with mass spectrometer detector)
   - Limit GCxGC outlet flow rate to ≤ 3 sccm to minimize mass spec pumping

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GC Peak Capacity ~ 1/(False Alarm Rate)

- Alternative (non GC) detector technologies exist for various classes of toxic vapors
- Several of these succeed in terms of:
  - •Detection sensitivity for individual target compounds
  - •Form factor, detection speed, battery life
- *They often fail due to large false positive detection rates in complex environments*

- Consider the worst case chemical analysis scenario:
  - Complex mixtures of completely random compounds of different classes
  - No chemical selectivity in sample collection or eluent detection, so that the entire burden of target identification falls on the GC separation stage.

- Statistical analysis by Davis and Giddings (Analytical Chem. **55**(1983)418.) To achieve:
  - 90% probability of single peak separation

Would require:

  - 95% ***unused*** or ***"empty"*** GC peak capacity
- So for full separation, a mixture of ***only 30 compounds*** would require capacity

$$C_p = 1/(1-0.95) \times 30 = 600$$

- Doing this separation in 1 min would require peak capacity production of at least 10 peaks/sec

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Micro Gas Analyzer Development

COTS GCxGC-MS

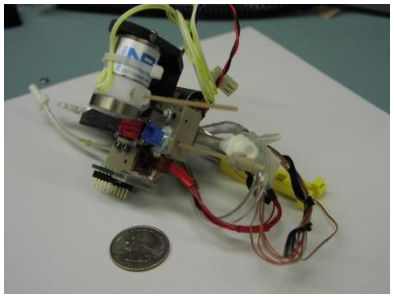
V ~ 2 m^3
t ~ 10^3 sec
P ~ 2 kW, E ~ 7 MJ
GCxGC
Peak capacity ~ 10^3

Peaks/sec ~ 1

Sandia handheld GC-SAW

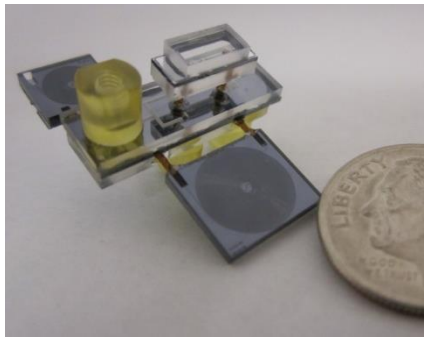
V ~ 1000 cm^3
t ~ 10^2 sec
P ~ 2W, E ~ 100J
Single GC
Peak capacity ~ 10
Peaks/sec ~ 0.1
(low FAR by limiting target chemistry)

Micro Gas Analyzer



Phase II
Single GC
V<20 cm^3

Phase IV
V<4cm^3
(Analytical components only)



t ~ 4 sec
E goal < 1J, actual 10-100J
GCxGC
Peak capacity > 300

Peaks/sec ~ 50

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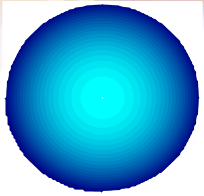
Column Cross Section Effects



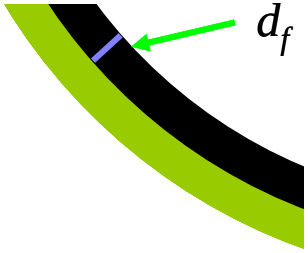
100 µm – round
7854 µm²

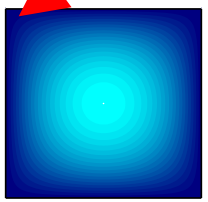
Round Cross Section

- Flow restriction and performance limited by radius
- Film deposition is uniform

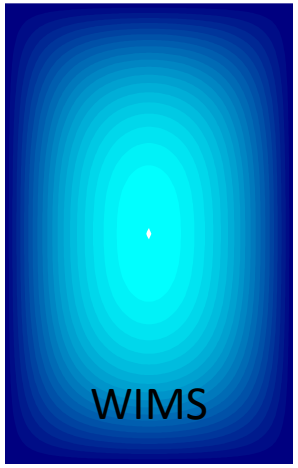
Rectangular Cross Section

- Flow restriction controlled by height
- Performance limited by width
- End effects
  - Film deposition often results in thicker phases in the corner
  - Thicker stagnant flow regions in corners

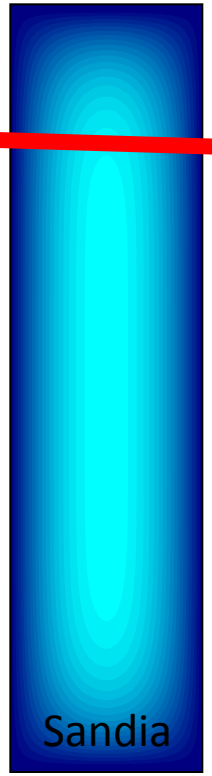




100 µm x 100 µm
10,000 µm2

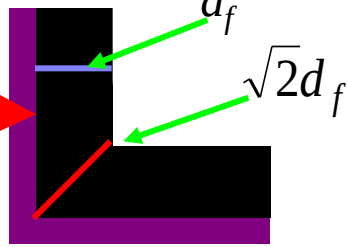


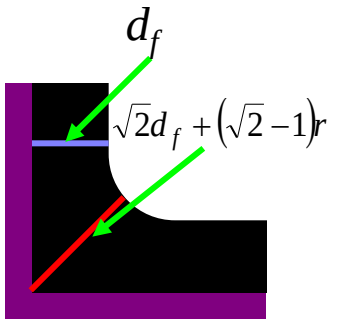
140 µm x 250 µm
35,000 µm2



100 µm x 400 µm
40,000 µm2

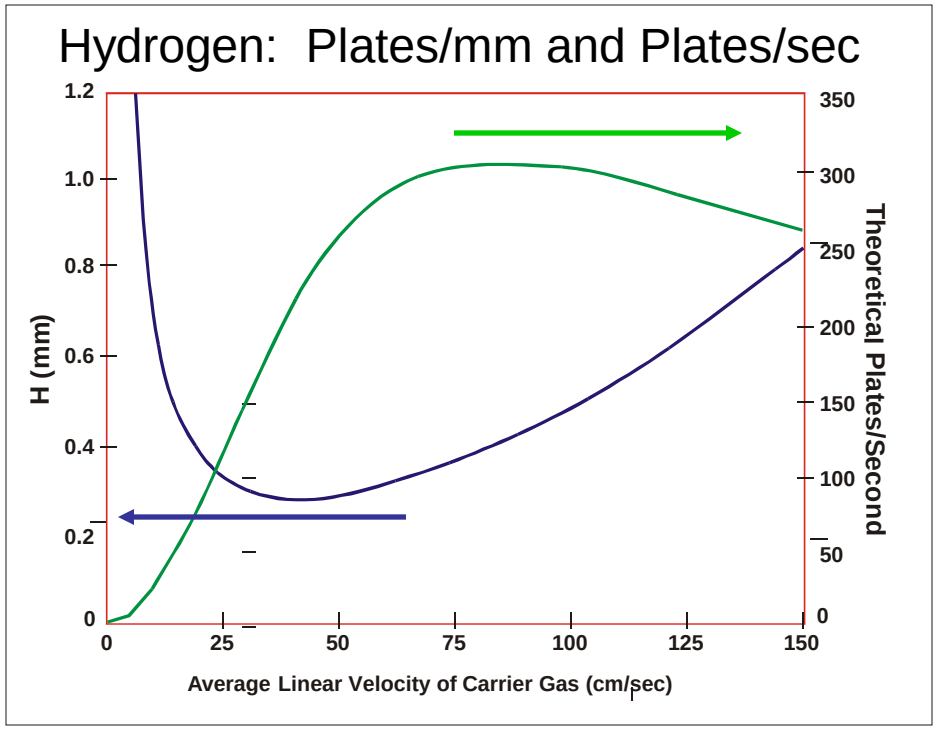
30 µm x 685 µm
20,550 µm2
DARPA





Why Use Rectangular GC Columns?

IF: Column efficiency is controlled by channel width, w (small);
And: flow resistance can be kept low by increasing channel height, h;
THEN: Columns can operate at linear flow velocities higher than the usual $\bar{U}_{opt}$ ("Golay minimum");
WHERE: Efficiency ***per unit time*** is optimized (see figure);
WITHOUT: Large increases in p_{inlet}, which require increased energy use and more stringent valve performance.



After fig. 5.16 in Analytical Gas Chromatography, 2nd edition, W. Jennings, E. Mittlefehldt, and P. Stremple, Academic Press (San Diego) 1997.

Other engineering advantages for portable GC applications:

- "Easy" variation of dimensions by Si etch processes
- Tight "wrapping" of columns, e.g. 1m/cm^2, reduces heat capacity for fast temperature programming

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Golay Equation for Performance of Rectangular GC Columns

B/ū

Cū

Extra-column connections

$$H = \underbrace{\frac{2D_g f_1 f_2}{\bar{u}}}_{\text{Longitudinal diffusion}} + \underbrace{\frac{\left(1+9k+25.5k^2\right)}{105(k+1)^2}\frac{w^2}{D_g}\frac{f_1}{f_2}\bar{u}}_{\text{Mass Transport in the Mobile Phase}} + \underbrace{\frac{2}{3}\frac{k}{(k+1)^2}\frac{(w+h)^2 d_f^2}{D_s h^2}\bar{u}}_{\text{Mass Transport in the Stationary Phase}} + \underbrace{\frac{\Delta t^2 \bar{u}^2}{L(k+1)^2}}_{\text{Extra-Column Band Broadening}}$$

$\bar{u}$ – average linear carrier gas velocity

D_g – binary diffusion coefficient in gas phase

f_1 –Giddings-Golay gas compression correction factor

f_2 – Martin-James gas compression correction factor

k – retention factor

w – channel width

h – channel height

d_f – stationary phase film thickness

D_s – binary diffusion coefficient in stationary phase

Δt – time correlating to extra column band broadening

L – column length

1. M.J.E. Golay, in ***Gas Chromotography 1958*** (Amsterdam Symposium), D.H. Destry, ed., Butterworths (London, 1958) pp. 139-143.
2. M.J.E. Golay, J. Chromatogr. 216 (1981) 1.

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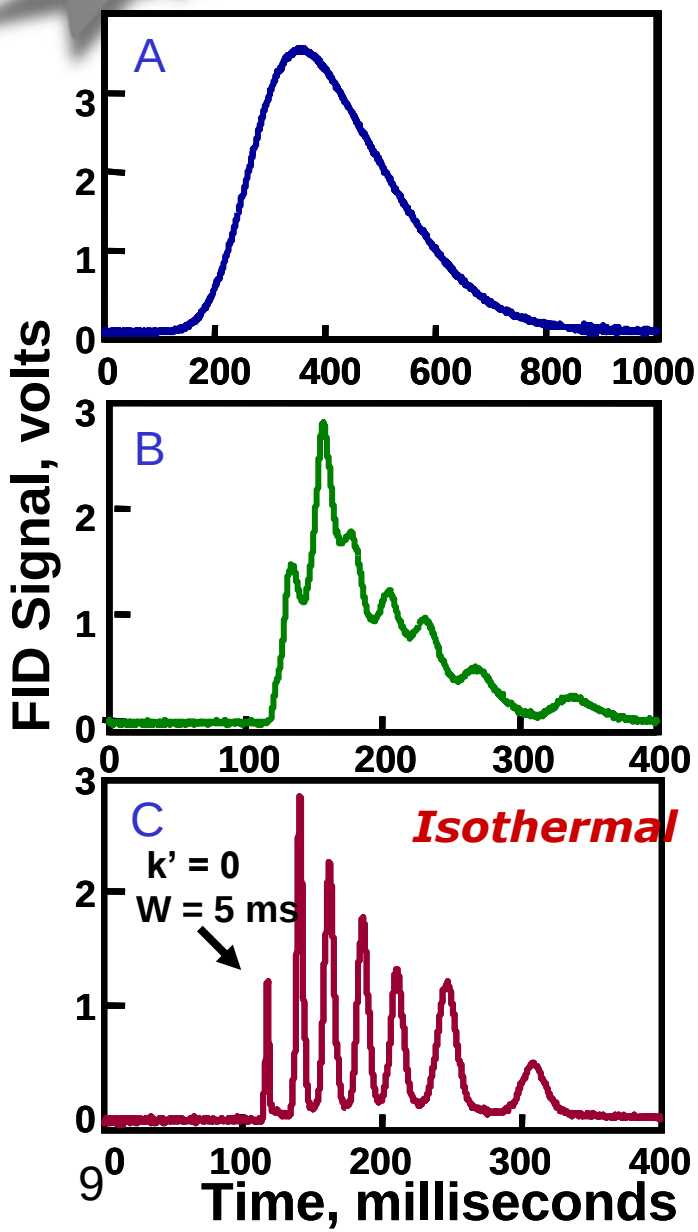
At High Speeds, Sample Injection Dominates Over Column Performance



Synovec et al. have demonstrated fast GC using COTS columns and high speed injection via fast valves and/or cryofocusing: cf. G.M. Gross, B.J. Prazen, J.W. Grate, R.E. Synovec, Anal. Chem. **76** (2004) 3517-3524.

- Example: Three types of injection under identical separation conditions (1 m x 100 µm column)
- Same 7-component mixture injected. Retention order: methanol, benzene, octane, chlorobenzene, anisole, decane, butylbenzene

(A) standard primary autoinjector

(B) single valve sample injector (20 ms)

(C) synchronized dual valve injector (2.5 ms)

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Flow-Modulated GCxGC Separations

Why do it?

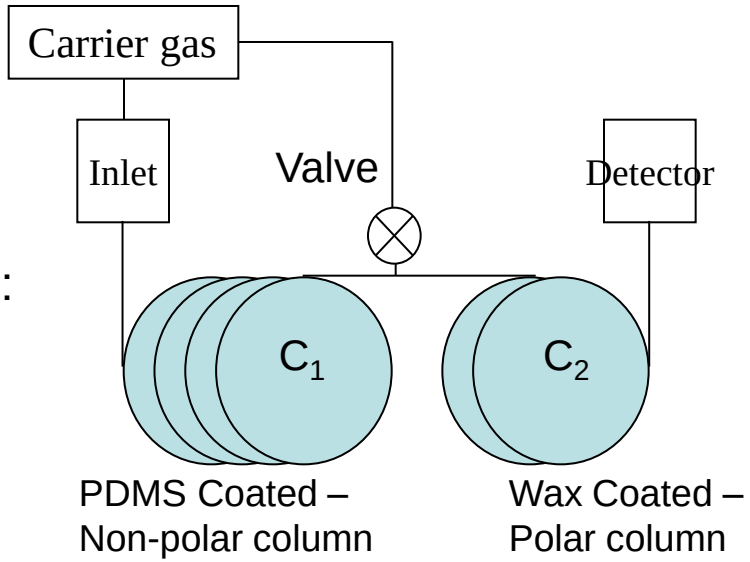
- By using two different stationary phases in series, different retention properties of the analytes are exploited

How it works:
(We're modulating flow, instead of retention index)

$$u_{i,z} = u_z/(k_{i,z} + 1)$$

- We cannot afford cryogenic gases in a portable system, so we modulate gas flow instead of k
- Saves power, weight, and complexity at the cost of lost refocusing of analytes onto C2

Stop-flow schematic:



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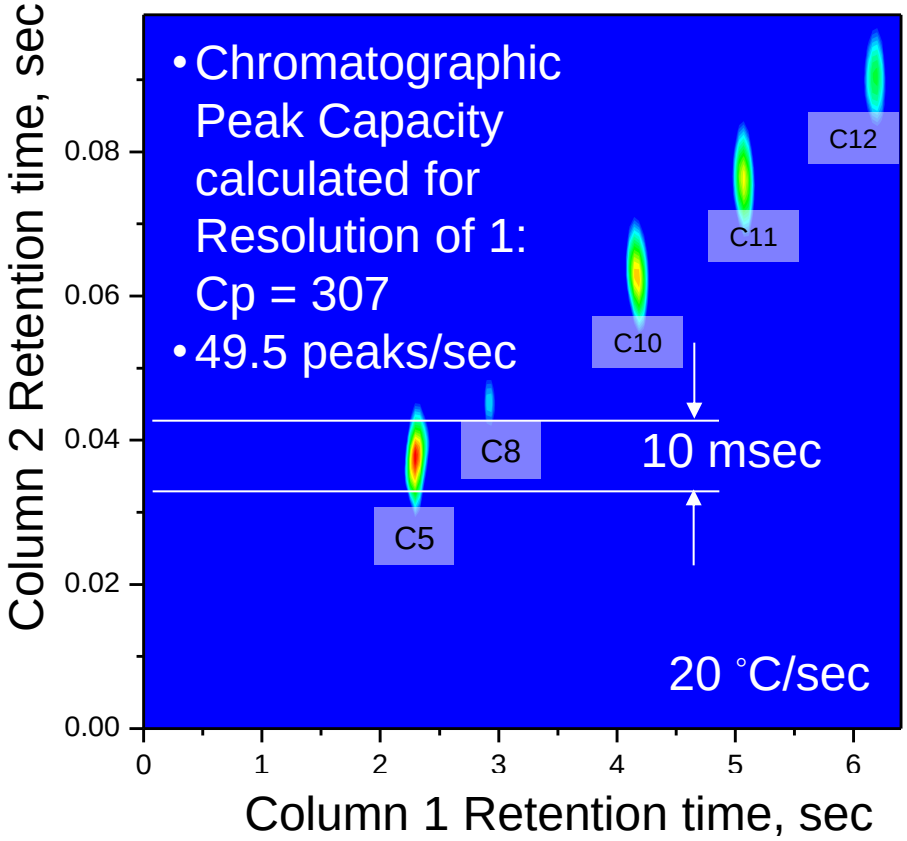
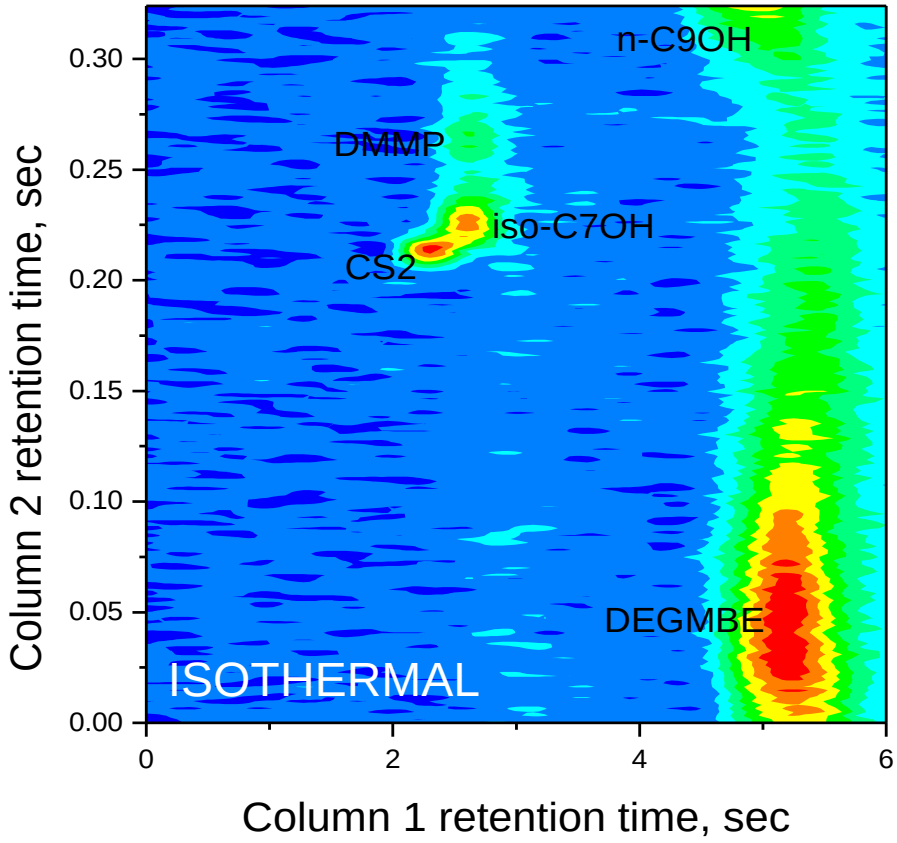
Rectangular Microcolumn GCxGC Results

Peak capacity estimated using alkane series and FID

Column 1 = Σ(Trennzahl numbers) = 30.63
Column 2 = mean isothermal Cp = 10.02



CW simulant separated from polar interferents. Detector is a coated NEMS resonator sensor (Caltech).



•Both used COTS sample injector **with high split ratio** and 2 sec "dead time"

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GC Sample Injection Requirements -or- Why use MEMS?

- Fast GC separations require narrow sample injection pulse widths

  (in the absence of on-column sample refocusing, which typically requires temperature modulation capability that exceeds the energy budget for battery operated systems)

- Large injection split ratios are unacceptable for field instruments that have trace analytical requirements and limited sample acquisition times. Total collected sample mass can be in the pg range.
- Convective flow "sweep time" for a splitless injector depends on local gas flow rate and the volume of the injector:

$$\Delta t \sim \frac{\{\text{volume of sample collector } (m^3)\}}{\{\textbf{\textit{local}} \text{ gas volumetric flow rate } (m^3/sec)\}}$$

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Golay Equation: The Extra-column Term

$$H = \underbrace{\frac{2D_g f_1 f_2}{\bar{u}}}_{\text{Longitudinal diffusion}} + \underbrace{\frac{\left(1+9k+25.5k^2\right)}{105(k+1)^2}\frac{w^2}{D_g}\frac{f_1}{f_2}\bar{u}}_{\text{Mass Transport in the Mobile Phase}} + \underbrace{\frac{2}{3}\frac{k}{(k+1)^2}\frac{(w+h)^2 d_f^2}{D_s h^2}\bar{u}}_{\text{Mass Transport in the Stationary Phase}} + \underbrace{\frac{\Delta t^2 \bar{u}^2}{L(k+1)^2}}_{\text{Off-Column Band Broadening in interconnects}}$$

Only 1 term is quadratic in ū … so extra-column broadening dominates at high speeds!

L = column length, which cannot be increased without increasing the analysis time

k = retention factor, determined by the analyte and stationary phase chemistries

Δt = time correlating to extra column band broadening

$\Delta t \sim$ {volume of extra-column interconnect (m^3)}
{***local*** gas volumetric flow rate (m^3/sec)}

High-speed performance + low injection split ratio requirement → small interconnect dimensions…

This drives the MEMS design for our MGA system!

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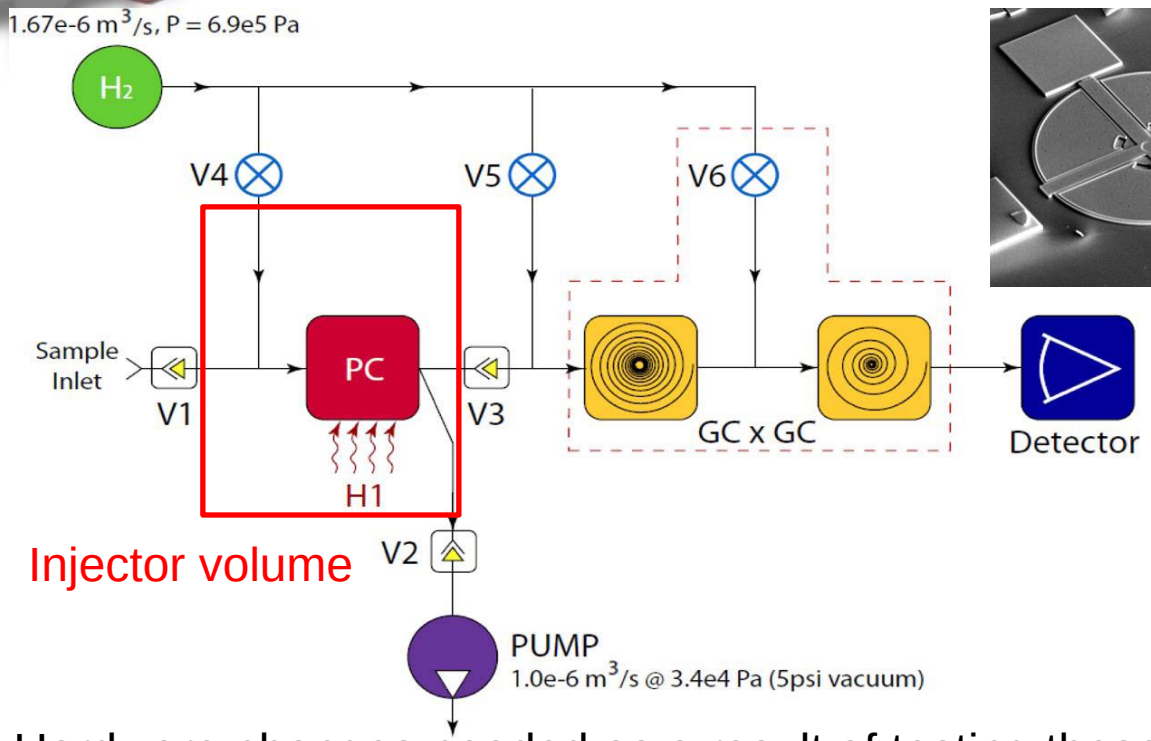
“Micro” Portable GC Instrument.1.



Microfabricated valves define the volume of a splitless injector (~5 µL) for high speed flow-modulated GCxGC

P. Galambos, et al., Journal of Microelectromechanical Systems **20(5)** (2011) 1150 – 1161.

- Hardware changes needed as a result of testing these devices:

1. Flow through V6 pathway is insufficient to completely stop GC1 flow using a single pressure source: Need separate V5 and V6 gas inlets.
2. V1 and V2 valve arrays prone to low yield and particle contamination (16 valve arrays).
3. Injector volume needs further reduction if flow rate at PC is to be reduced by customer’s 3 sccm column flow requirement. (Column flow sets linear flow velocity at PC during injection.)

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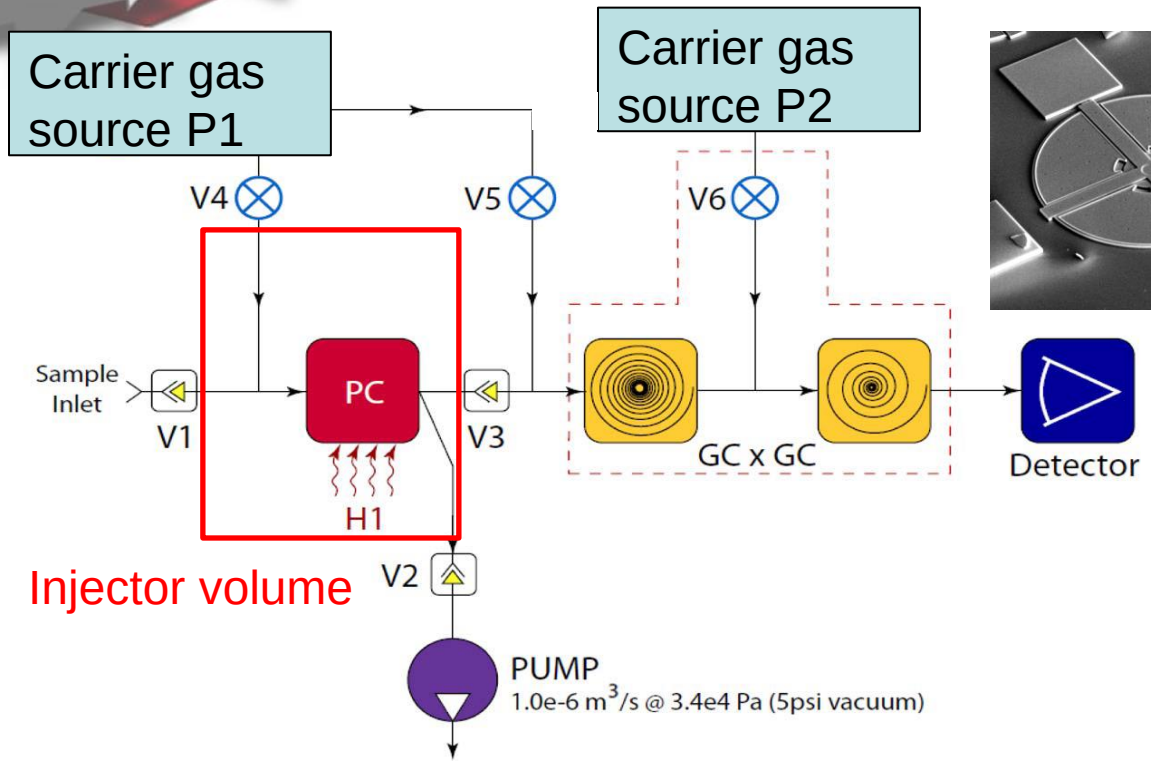
"Micro" Portable GC Instrument.2.



Microfabricated valves define the volume of a splitless injector (~5 µL) for high speed flow-modulated GCxGC

P. Galambos, et al., Journal of Microelectromechanical Systems **20(5)** (2011) 1150 – 1161.

- First design change: Provide separate carrier gas inlets at V5 and V6, so that modulation (V6 open) will fully stop the flow on GC1.

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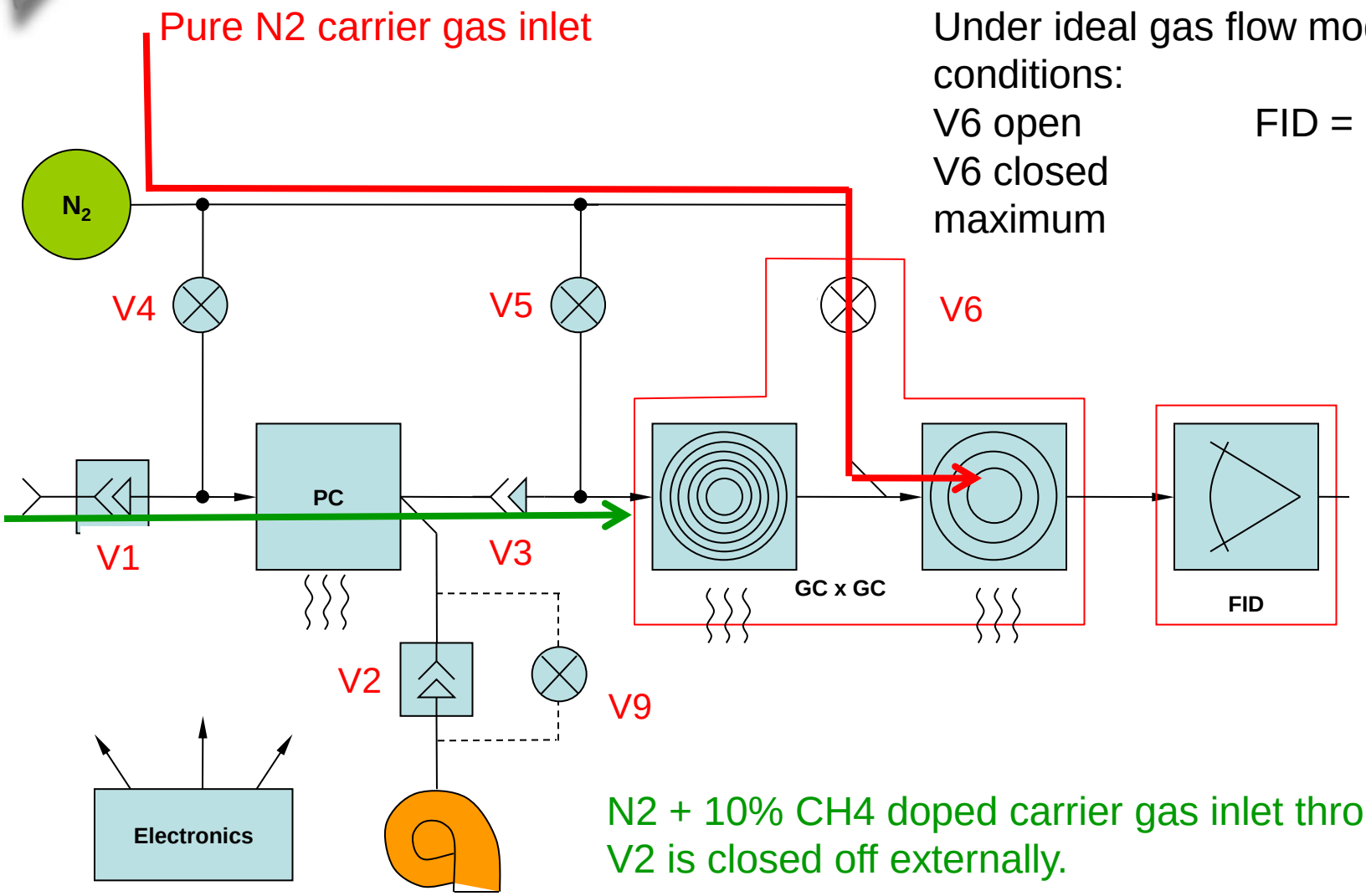
Modulation Flow Test: CH_4 Tracer Gas



Under ideal gas flow modulation conditions:

V6 open FID = 0

V6 closed FID = maximum

N2 + 10% CH4 doped carrier gas inlet through V1.
V2 is closed off externally.

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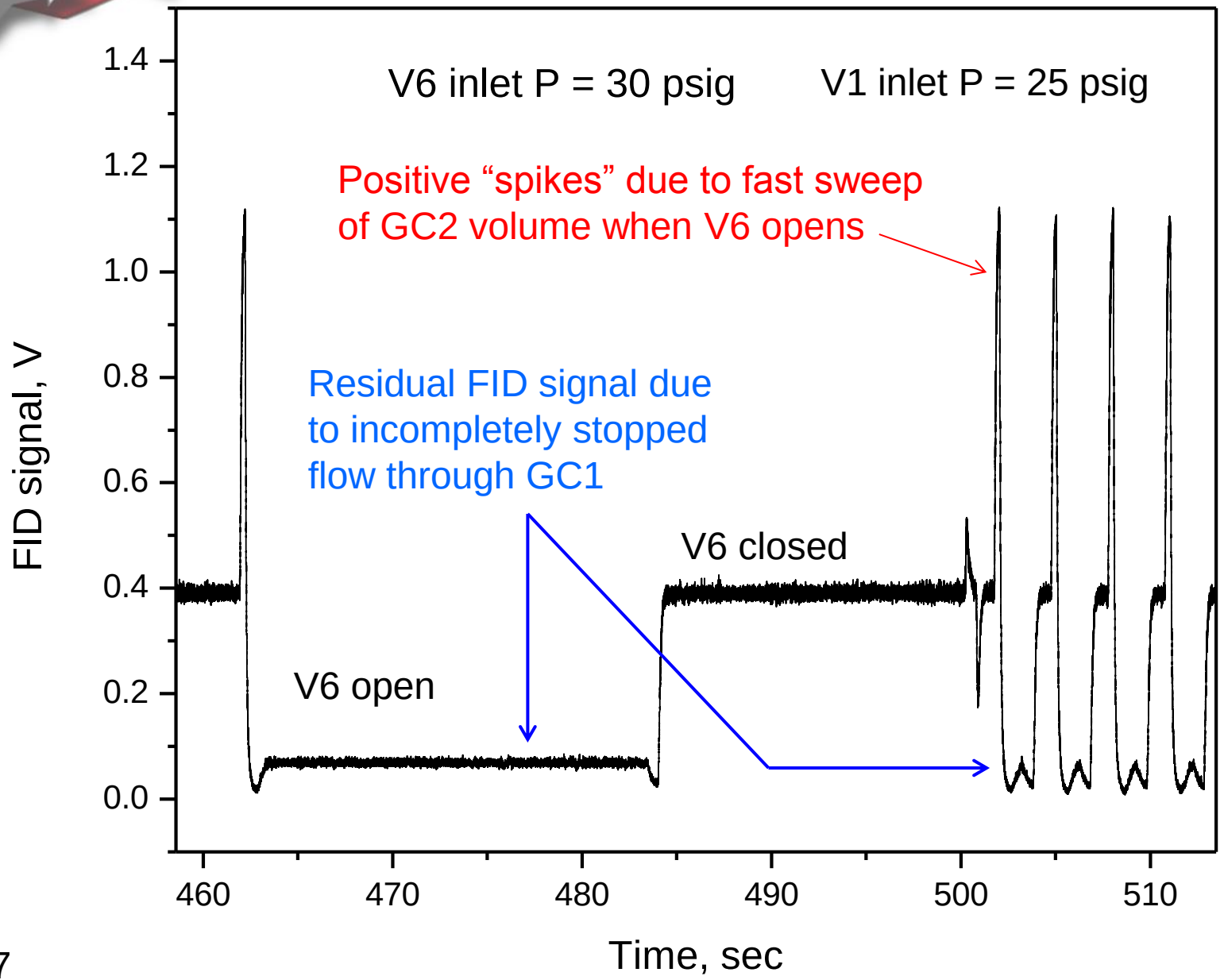
Modulation Flow Test: $\Delta P = 5$ psi



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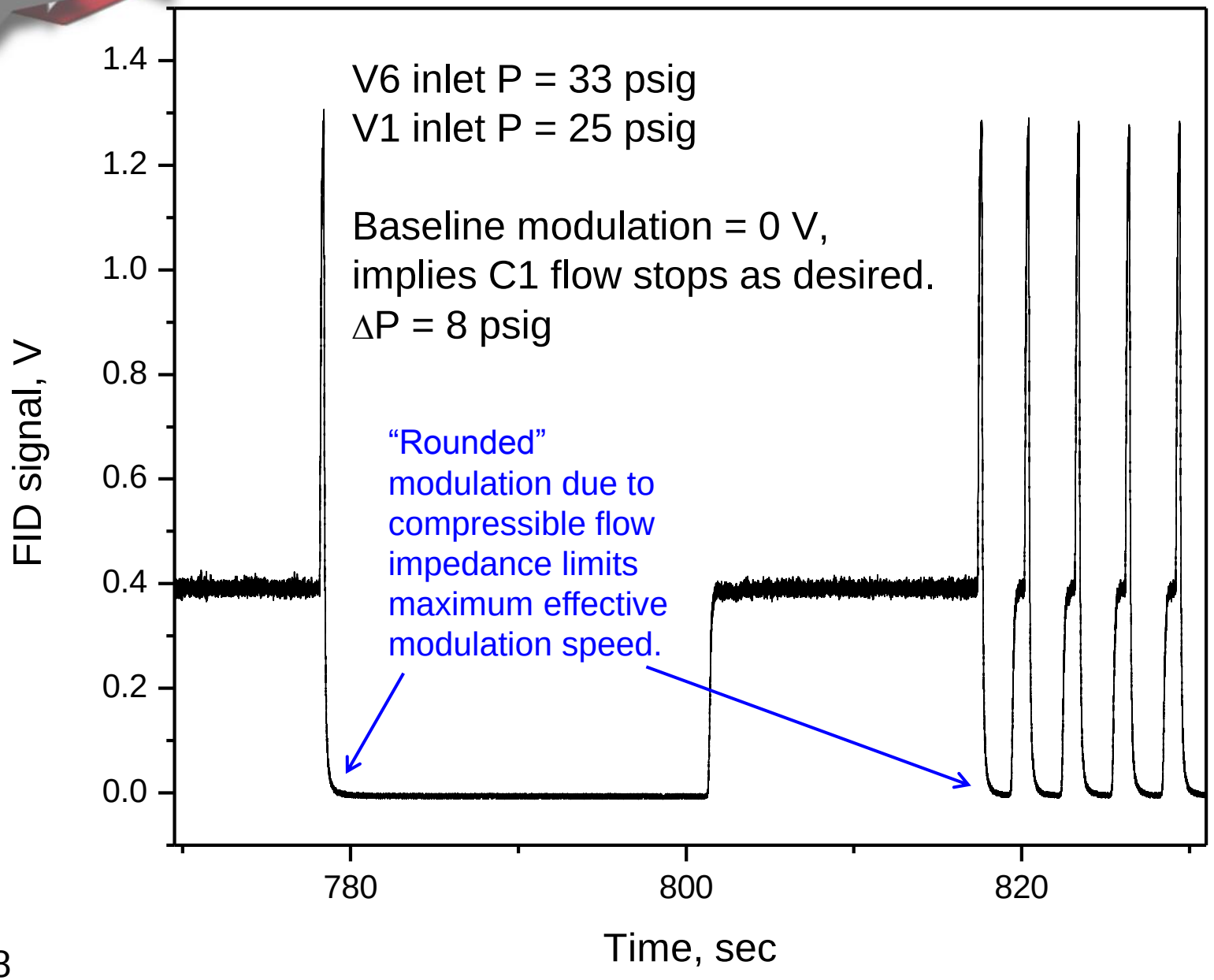
Separate Inlet P Enables Full Stop-Flow Modulation



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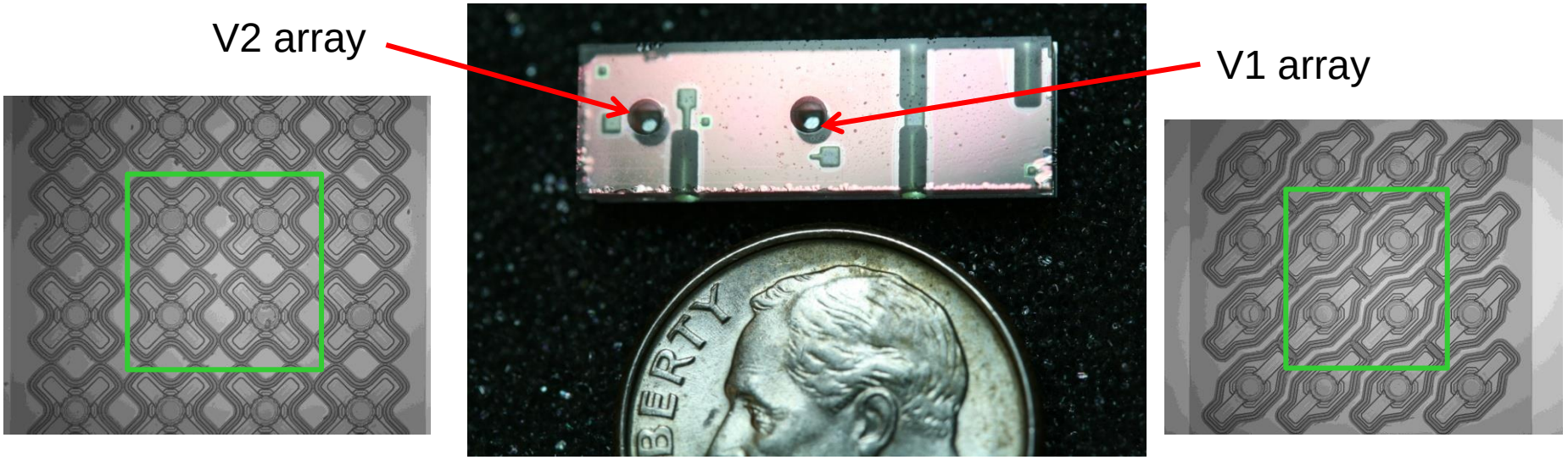
Design Changes for Higher Yield

- Old: 4 sec cycle time, 60 sccm sample air flow rate at ΔP = 2.5 psi
  - Required 16 micro valves in parallel for air sampling (PC inlet and outlet)
- New: 60 sec cycle time (slower GC flow)→ reduce sample air flow to 15 sccm
  - Reduce inlet and outlet valve arrays from 4x4 to 2x2



- Anticipated yield improvement between Valve Module versions 1 and 2:

1. VM1 used 36 microvalves. Module yield = 25%. Individual valve yield estimate = $(0.25)^{1/36} = 0.962$
2. Eliminating 24 of 32 valves in V1 and V2 array (as described above) and moving V5 and V6 off chip (not shown) gives VM2 a total of 10 microvalves.
3. Assuming individual valve yield is unchanged, VM2 yield should be $(0.962)^{10} = 68\%$

3rd System Design Change: Reduce GCxGC Outlet Flow

- Goal: Integrate PC-GCxGC system with a mass spectrometer detector
  - Micro GC capable of useful m/e resolution at 1 Torr operating pressure for ionizer and mass filter (Prof. J.M. Ramsey, et al., U. of N. Carolina)

- In order to reduce vacuum pumping requirements at the detector, the current system design goals include the following constraints and targets:
  - Air carrier gas outlet flow ≤ 3 sccm
  - t_R of critical target compounds ≤ 1 minute
  - GCxGC peak capacity ≥ 300/min, or Cp/t > 5/sec, i.e., average peak width at baseline ≤ 200 msec.

- Our approach: Model rectangular GC column performance, seeking column dimensions that will balance tradeoffs between:
  - Gas flow rate
  - Performance (Cp/t)
  - Practical manufacturing constraints, i.e., aspect ratio available for deep reactive ion etch process in Si micro columns

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Golay, Giddings, and Guiochon equation for rectangular columns[1,2,3]

$$H = \underbrace{\frac{2D_g f_1 f_2}{\bar{u}}}_{\text{Longitudinal diffusion}} + \underbrace{\frac{\left(1+9k+25.5k^2\right)}{105(k+1)^2}\frac{w^2}{D_g}\frac{f_1}{f_2}\bar{u}}_{\text{Mass Transport in the Mobile Phase}} + \underbrace{\frac{2}{3}\frac{k}{(k+1)^2}\frac{(w+h)^2 d_f^2}{D_s h^2}\bar{u}}_{\text{Mass Transport in the Stationary Phase}} + \underbrace{\frac{\Delta t^2 u_o^2}{L(k+1)^2}}_{\text{Extra-Column Band Broadening}}$$

$\bar{u}$ – average linear carrier gas velocity

u_o – outlet linear carrier gas velocity

D_g – binary diffusion coefficient in gas phase

f_1 –Giddings-Golay gas compression correction factor

f_2 – Martin-James gas compression correction factor

k – retention factor

w – channel width

h – channel height

d_f – stationary phase film thickness

D_s – binary diffusion coefficient in stationary phase

Δt – time correlating to extra column band broadening

L – column length

1 - Golay MJE. Theory of Chromatography in Open and Coated Tubular Columns with Round and Rectangular Cross-Sections. Gas Chromatography. New York:Academic Press; 1958;36-55

2 - Giddings JC, Chang JP, Myers MN, Davis JM, Caldwell KD. Capillary liquid chromatography in field flow fractionation-type channels. *J Chromatography A*. **1983**;255:359-379

3 - Gaspar, G.; Annino, R. Vidal-Madjar, G.; Guiochon, G. *Anal. Chem.* **1978**, *50*, 1512

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Model Evolution

Effect of Aspect Ratio, Film Thickness Correction

Ahn and Brandani Model – AIChE Journal, Dec. 2005

$$H = \frac{2D_g f_1 f_2}{\bar{u}} + \frac{\left(A + Bk + Ck^2\right)}{96(k+1)^2}\frac{w^2}{D_g}\frac{f_1}{f_2}\bar{u} + \frac{2k}{3(k+1)^2}\frac{d_{fc}^2}{D_s}\bar{u} + \frac{\Delta t^2 u_o^2}{L(k+1)^2}$$

$$A = \frac{32}{35}\left[\frac{6.192(\alpha-1)^2}{(\alpha-0.1)^2} + 1.759\right]$$

α = aspect ratio (always ≥ 1)

$$B = \frac{64}{35}\left[\frac{6.192(\alpha-1)^2}{(\alpha-0.1)^2} + 1.759\right] + \frac{32}{5}\left[\frac{3.213(\alpha-1)^2}{(\alpha+0.2)^2} + 0.938\right]$$

$$d_{fc}^2 = \frac{\alpha + 1 + \frac{2d_f}{w}}{\alpha+1} d_f$$

$$C = 16\left[\frac{2\alpha^2}{(\alpha+1)^2}\right] + \frac{32}{35}\left[\frac{6.192(\alpha-1)^2}{(\alpha-0.1)^2} + 1.759\right] + \frac{32}{5}\left[\frac{3.213(\alpha-1)^2}{(\alpha+0.2)^2} + 0.938\right]$$

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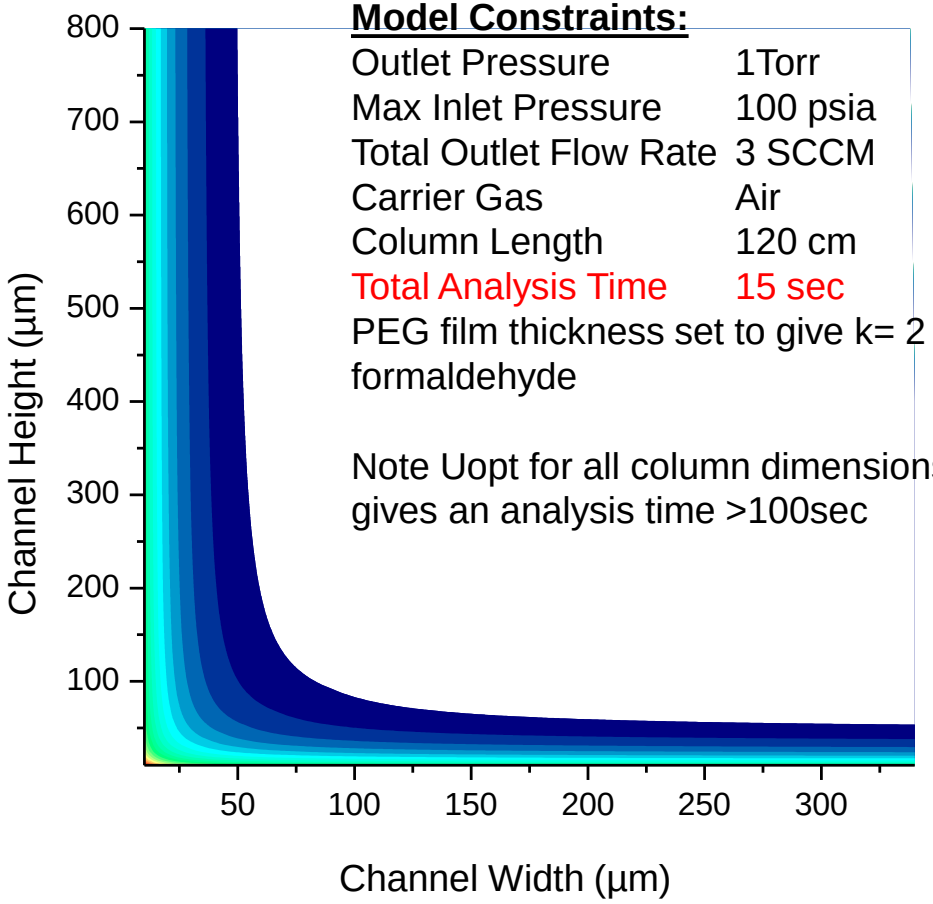
Model Result: 1D GC Isothermal Peak Capacity vs. Column Dimensions, With Constraints

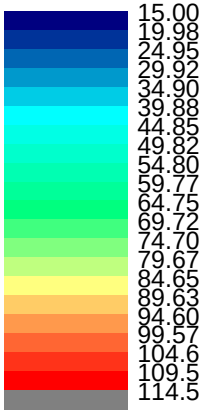


Model Constraints:

Outlet Pressure	1Torr
Max Inlet Pressure	100 psia
Total Outlet Flow Rate	3 SCCM
Carrier Gas	Air
Column Length	120 cm
Total Analysis Time	15 sec

PEG film thickness set to give k= 2 for formaldehyde

Note Uopt for all column dimensions gives an analysis time >100sec



Color bars represent total peak capacity achieved in 15 sec

Example: For 20 µm x 500 µm channel dimensions, Cp achieved under these constraints would be ~40.

Extending to 1 min elution time gives modeled Cp ~ 160.

Increasing analysis time by 4X (to 1 min) would:

- Increase theoretical plates, N, by ~4X
- Increase Cp by $\sqrt{N}$ ~ 2X
- For our example at 20 µm x 500 µm: Isothermal, 1D Cp/min ~ 80

- To achieve our target of Cp/min = 300 at the 3 sccm flow condition, we will need to "recover" a factor of 3X-4X in Cp/t over the model result, through use of GCxGC and T-programming.

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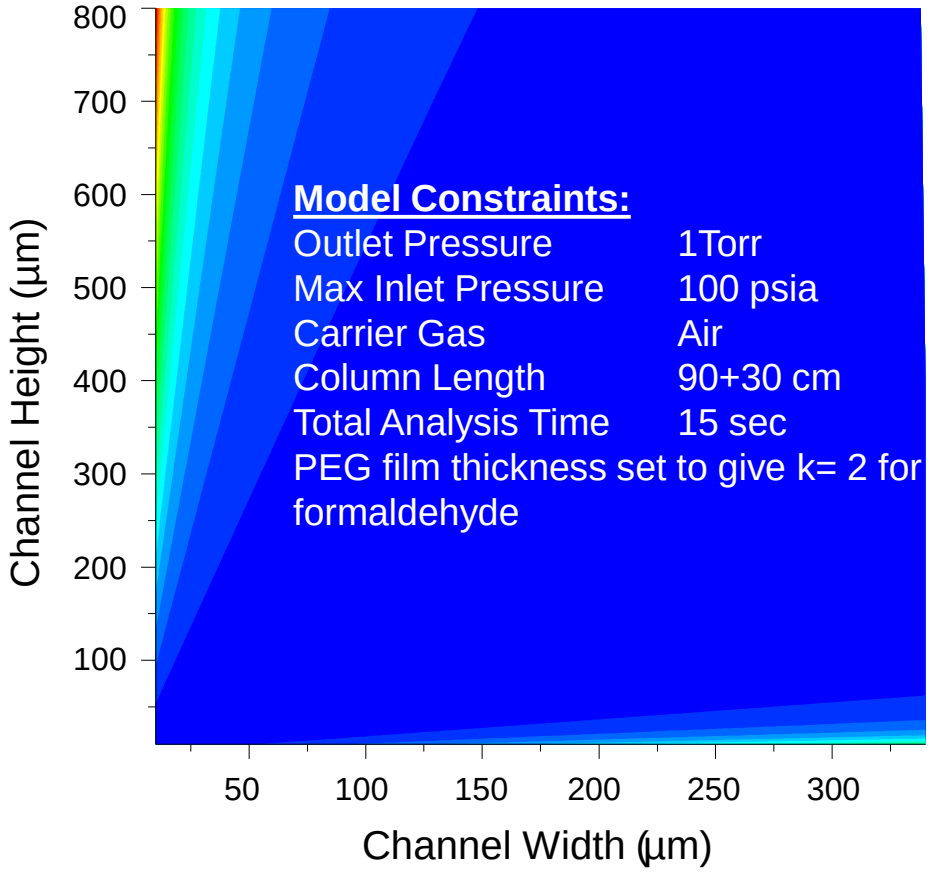
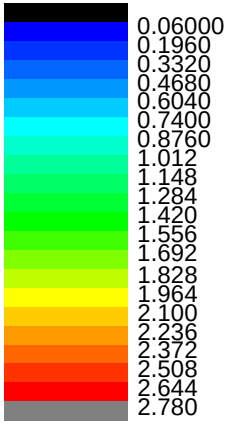
Modeled Average Outlet Flow Rate (sccm) vs. Column Dimensions: Assumes GCxGC 50% duty cycle





Color bars represent GCxGC outlet gas flow rate in SCCM

Example: For 20 µm x 500 µm channel dimensions, average gas flow under these constraints would be ~0.8 sccm.

- For our current column dimensions (30 µm x 685 µm) measured flow rates exceed model flows by up to ~ 3x
- Scaling to new dimensions (20 µm x 500 µm) allows a model safety factor to maintain flow < 3 sccm

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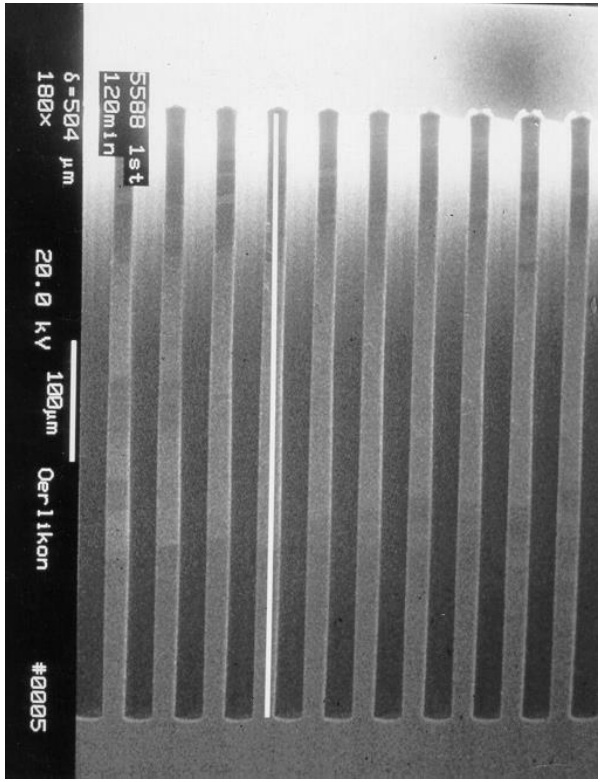
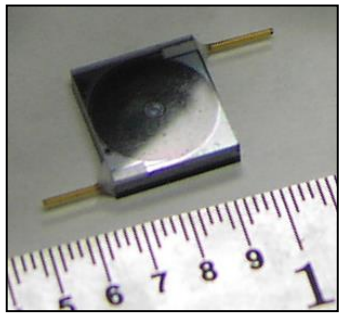
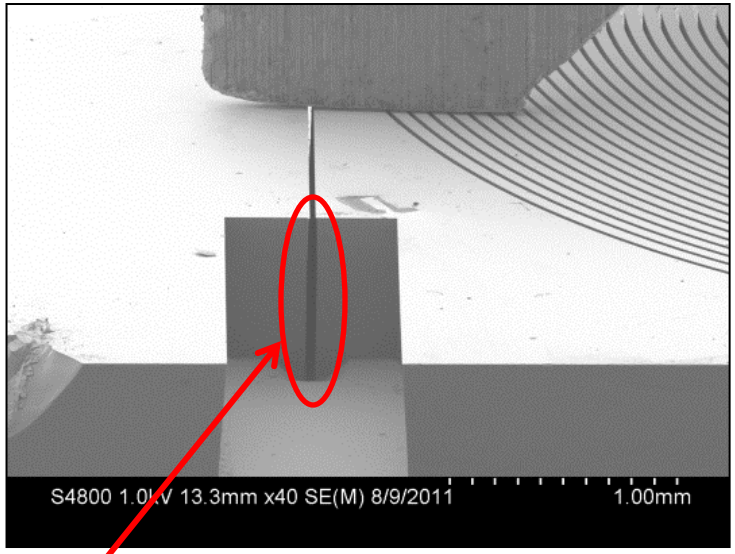
New Micro GC Column Dimensions





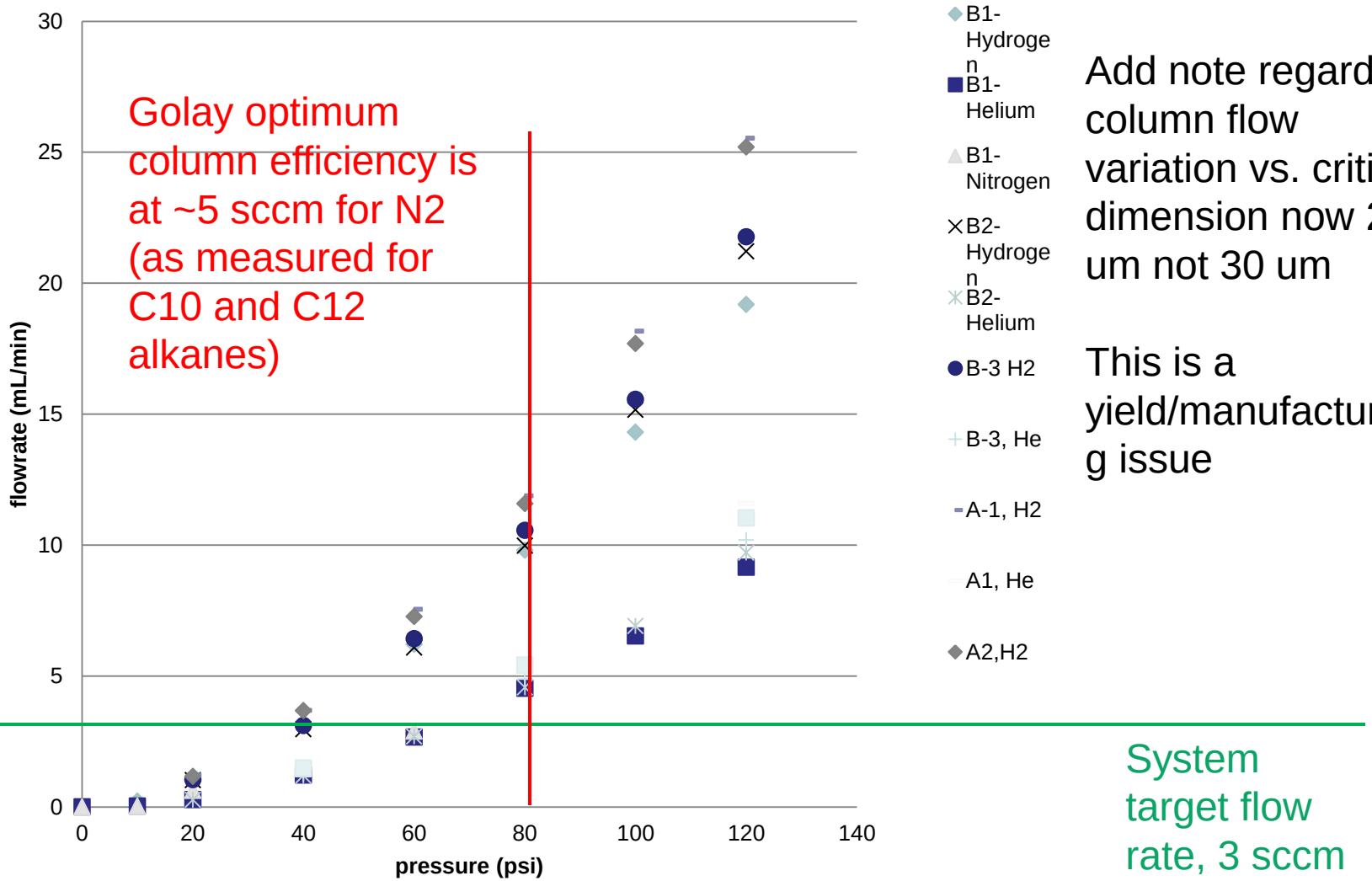
What's different?



- Column dimensions now 20 x 500 instead of 30 x 685 µm
- Column L = 1 m instead of 90 cm

- Aspect ratio of 25:1 at 20 µm critical dimension

Volumetric gas flow at outlet vs. inlet P for “20100” GC column using N2, He, and H2 carrier gases



Add note regarding column flow variation vs. critical dimension now 20 um not 30 um

This is a yield/manufacturing issue

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“20100” GC column results to date: Significance

- Goal of model was to select dimensions that enable Cp ~ 300 in 1 minute for GCxGC, with outlet gas flow constrained to 3 sccm. Assumptions were made in the model regarding carrier gas, analyte diffusion coefficient, analyte retention index, and stationary phase volume ratio.

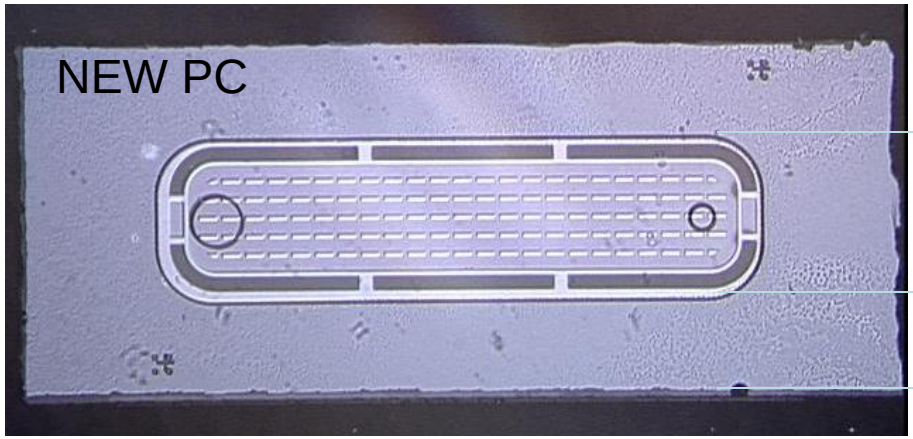
- Current results indicate that best column efficiency is found at 5-6 sccm rather than at 3 sccm
  - We may be able to affect this by changing phase volume ratio (modifying coating procedure).

- **The critical system issue: Restricting column flow increases sample injection peak width, which then restricts GC separation speed.**
  - Recall that extra-column effects dominate high speed GC performance.

  - Possible mitigation strategies:
  - Accept a sample split at the injector (increases system limit of detection)
  - Reduce system LOD by adding an ion multiplier at the Mass Spec? Increases system pumping requirements, reducing portability.
  - Reduce sample injection volume even further (reduce PC dimensions)
  - Possible microfabricated cryofocusing? (cf. Zellers, et al.)

Modified Preconcentrator

Die dimensions unchanged, 9 mm x 3.4 mm



PC volume reduced by factor of 1.76 (from 5 to 2.8 uL)

Surface area available for anodic bonding of bottom glass increased by 58%

Dominant PC failure mode in previous design was failure of bottom glass-Si bond, causing gas leaks

PC device yield increased from < 20% to approximately 75%

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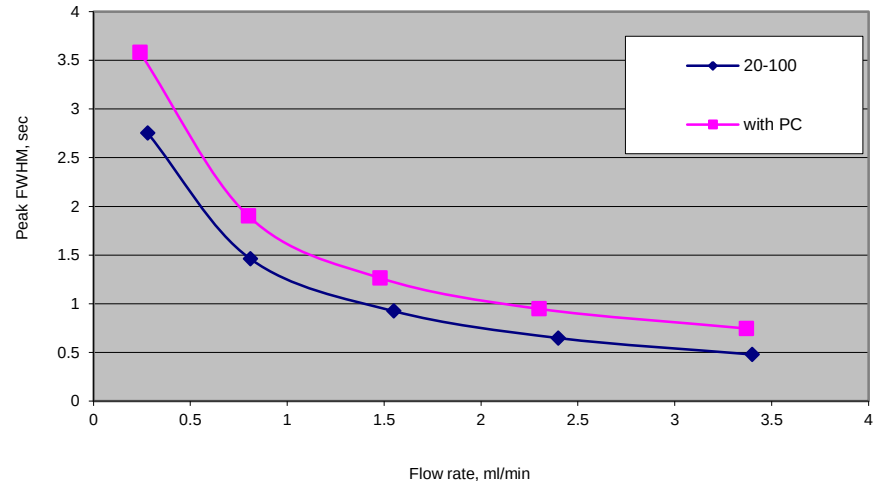
Preconcentrator Injection Peak Width vs. GC Outlet Flow

- Peak widths measured at FWHM for methane injection through columns at representative flow rates, with and without preconcentrators in the flow path.
- Note that methane results are “best case”: Dominated by convective flow and diffusion rates with no broadening due to chemical retention and PC desorption kinetics.

Methane peak width (avg of 3) vs flow rate N2 carrier

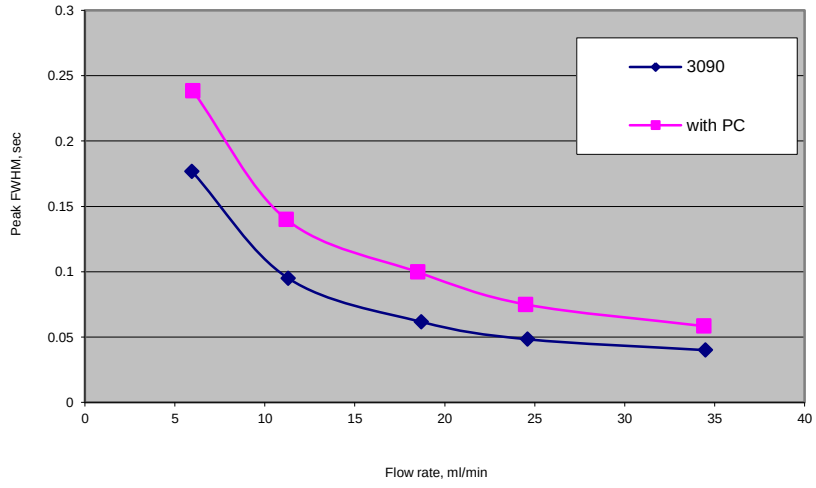
“New” column, 3 sccm N2 flow.



FWHM = 480 msec column only, 745 msec with PC

Methane peak width (avg of 3) vs flow rate H2 carrier

“Old” column, 35 sccm H2 flow.



FWHM = 45 msec column only, 58 msec with PC

- Injection peak width required to achieve our separation performance goal of Cp/t ~ 5 is 200 msec at baseline, or ~ 118msec FWHM.
- This target injection width was achieved with “old” columns at high flow, but not with new low flow columns.

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Microfabricated GCxGC System: Summary

- Our design utilizes high aspect ratio GC columns to maximize peak capacity production per unit analysis time, ***BUT***…

- **Sample injection, not on-column broadening, dominates fast GC performance**.

- We have designed a microvalve injector system to minimize injection peak width while maintaining splitless injection to maximize system sensitivity.

- System performance is closely coupled to operating constraints:
  - GC column dimensions have been optimized for Cp/t production at low carrier gas flow rates, in order to reduce mass spectrometer pumping requirements, ***BUT***…
  - Reducing volume flow at outlet greatly reduces linear flow velocity at inlet (preconcentrator), which in turn slows GCxGC separation speed.
  - To mitigate this, we need to:
  - Reduce PC volume even further.
  - Accept a split and/or higher column flow.
  - Refocus injection on column or on a micro cryofocusing component.

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