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Microfabricated Preconcentrators for Portable Chemical Analysis Systems

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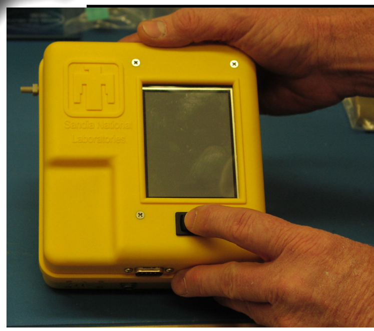
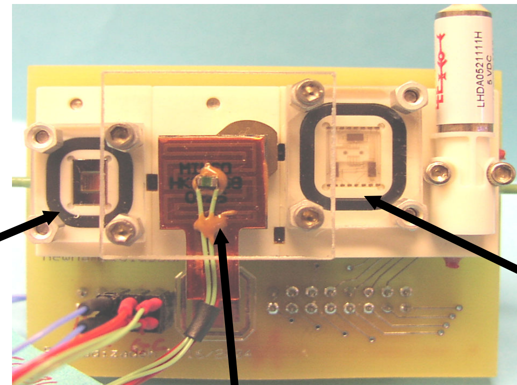
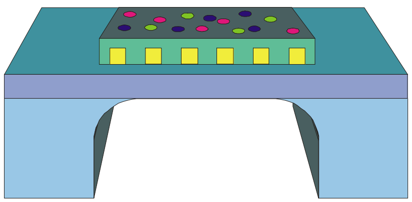
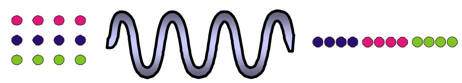
Sandia's MicroChemLab™

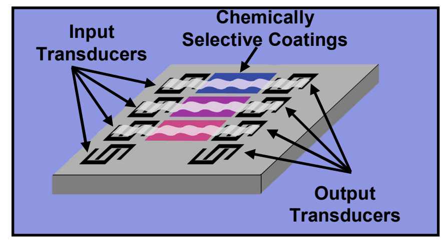
A hand-held chemical analysis system that uses three integrated modular components







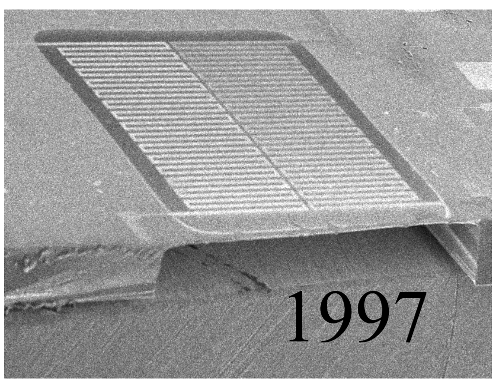


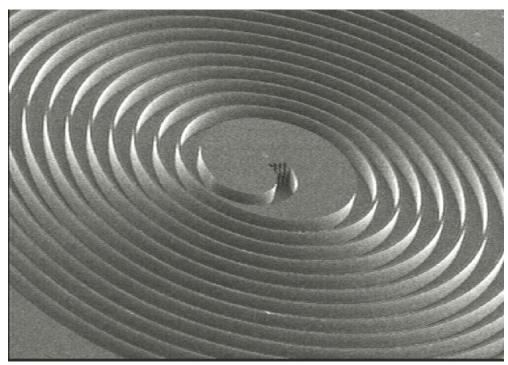


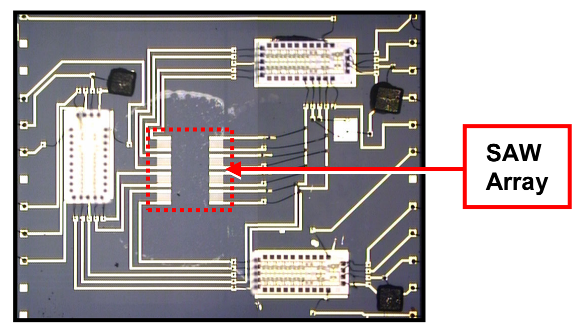
Preconcentrator accumulates analytes of interest

Gas Chromatograph separates analytes in time

Acoustic Sensors provide sensitive detection







US Patents: 6,171,378, 6,527,835

IEEE Sensors Journal, 6 (3) 784-795, 2006.

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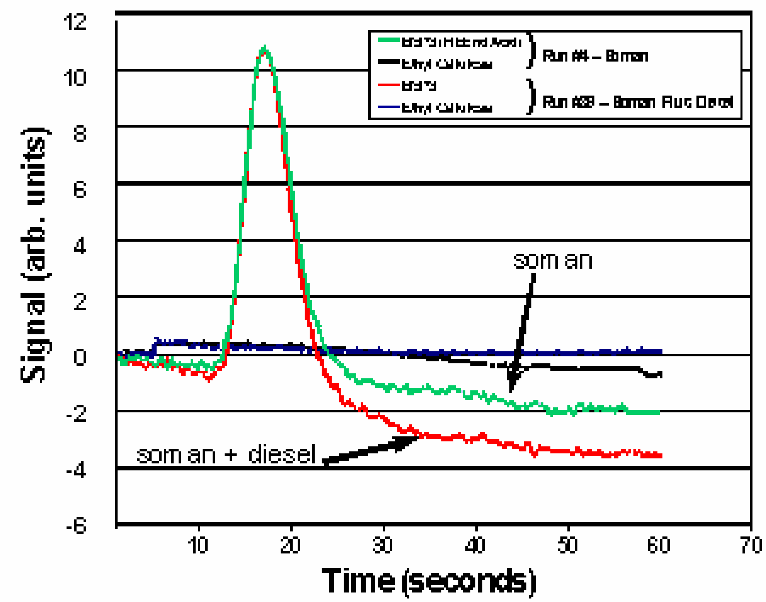
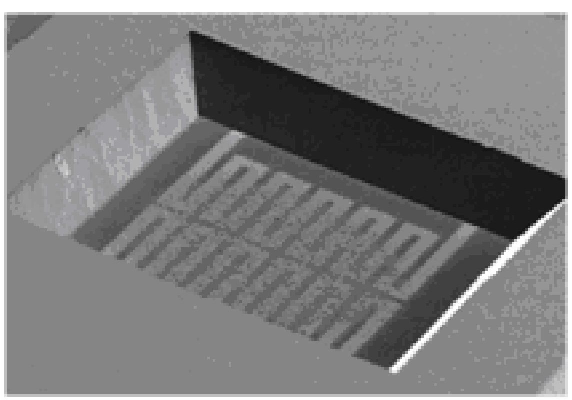
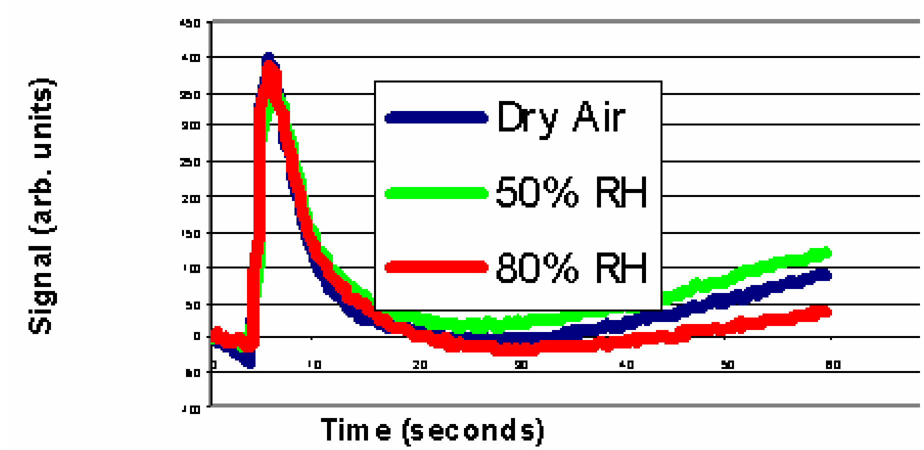
Planar MicroFabricated Preconcentrators

- **Low C, high efficiency adsorbent platform**
  - **2000°C/W; 10msec ramp**
- **Minimal flow restriction**
  - **5 psig, 200 mL/min**
- **Concentrate targets**
- **Reject interferants**
- **Rapid release - a non-mechanical GC injector**
- **Bosch or KOH etched to SiN**







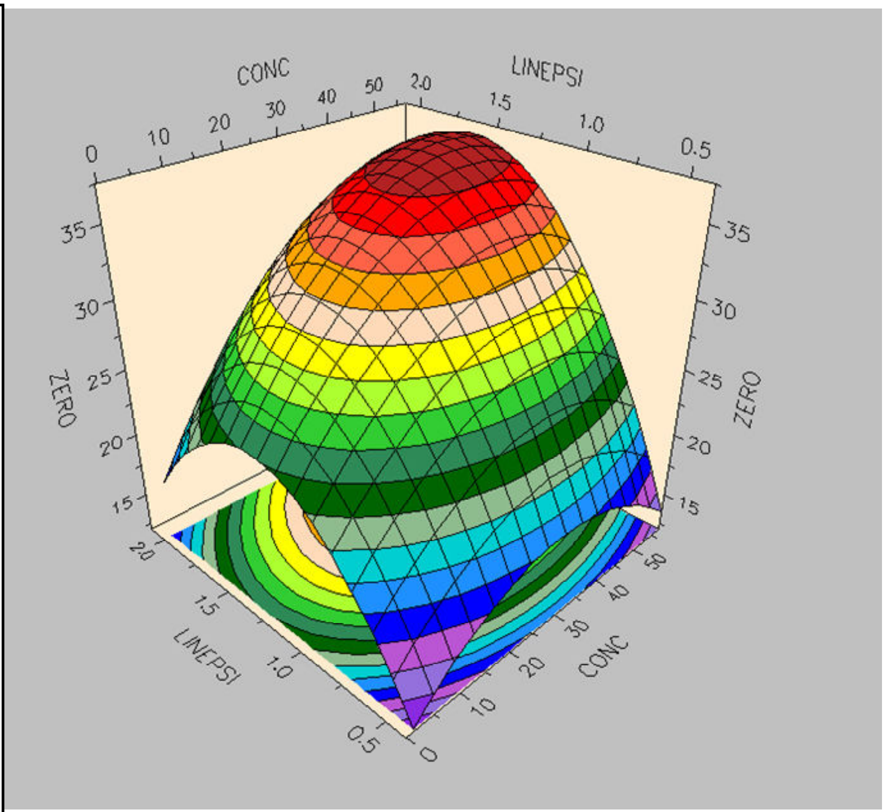
CFD Modeling and DOE

DOE

- Carboxen 1000 and light hydrocarbon
- Varied [C], collection time (tc), desorption flow (f), temperature (T) and desorption time (td)
- GC/FID Agilent 6890
- Statistica - full quadratic

Conclusions

- Peak area, Ap, increases with [C]
- Maximum in Ap with f
- Peak width, W, is not influenced by [C]
- W decreases with f
- Max in W with T
  - heated area increase, degradation
- Increased tailing with T
- Pe ~ convection/diffusion increases with f, [C] and decreases with T



R. J. Simonson, et. al., "Optimization of a Microfabricated Planar Preconcentrator," Proceedings of the 2nd Joint Conference on Point Detection for Chemical and Biological Defense, Williamsburg, VA 3/1-5/2004, Manuscript K1.

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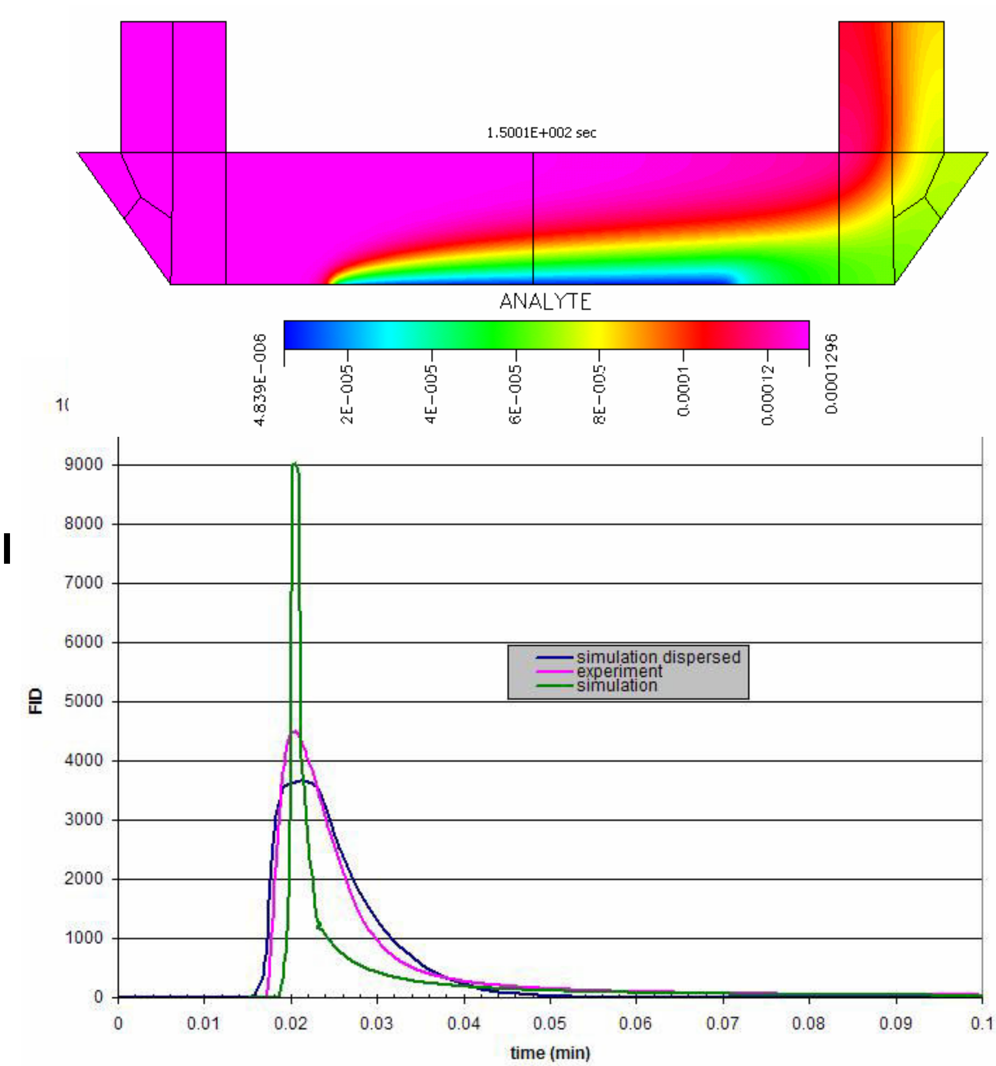
CFD Modeling (ESI Group) & DOE

- Computational Fluid Dynamics
- 2D – flow and adsorbent scaled
- Simplified thermal model
- Unity sticking
- Calibration on DOE
- Adsorption: A + s → A(s)
  - k = 36,500 s-1; 25,300 s-1 from Modified-Wheeler
- Desorption: A(s) → A + s
  - first-order Arhennius 30.1 kJ/mol
- Can predict other DOE runs
- Aris-Taylor Diffusion

- Diffusion is a dominant effect

- Did not predict fall off in Ap with f
  - Quadratic or simplicity of model; turbulence not an issue



R.P. Manginell, Sekhar Radharishnan, et. al., "Two-dimensional modeling & simulation of mass transport in microfabricated preconcentrators", accepted IEEE Sensors Journal.

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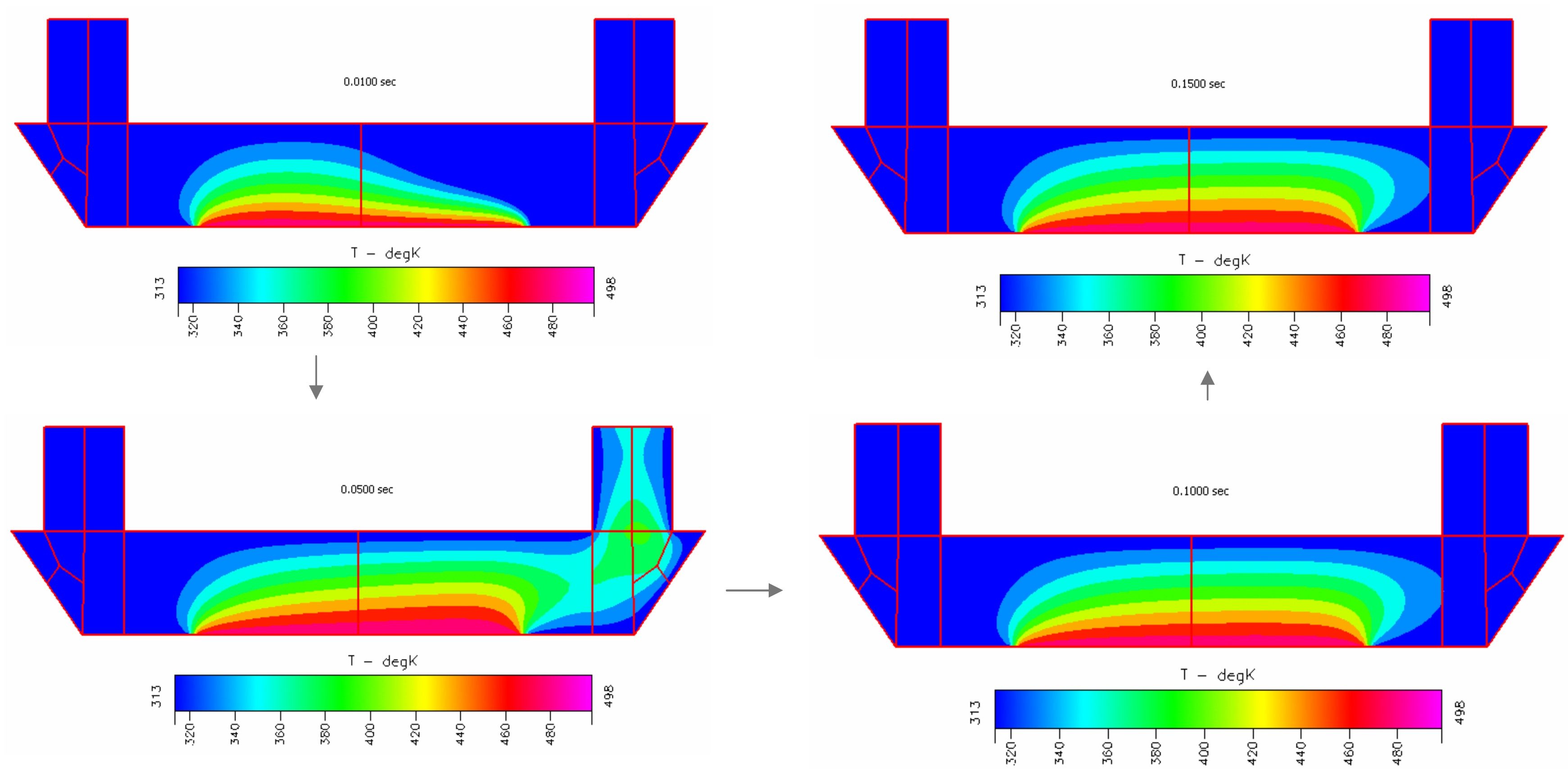
Eye Candy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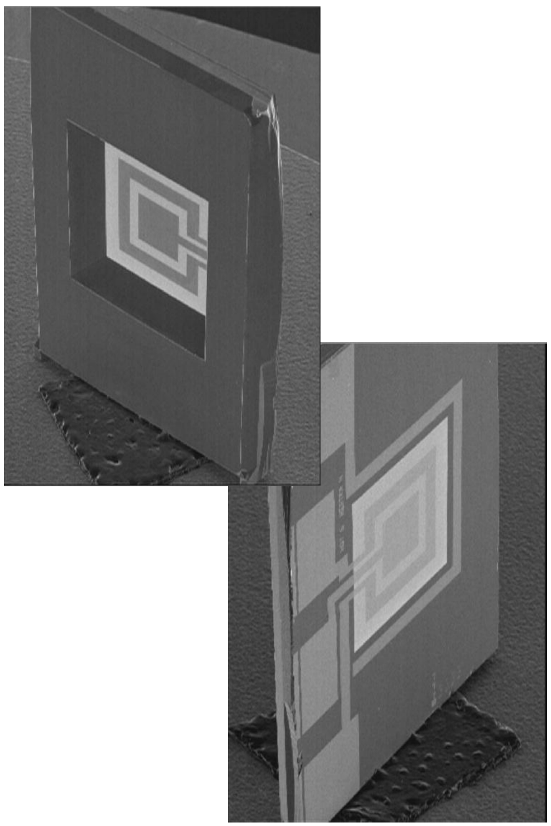
3DPCs as a supplement or replacement for the planar PC

Planar PC

1. Low C, high thermal efficiency
2. Fast response, low power
3. Collection limitations

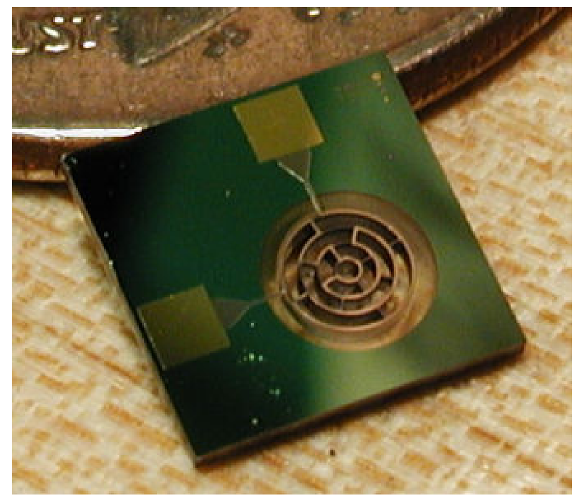
3DPCs

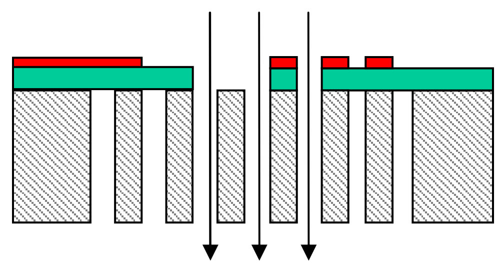
1. Planar PC items 1 & 2 retained
2. Smaller diffusion length, higher area, flow through
3. Pressure balance possible



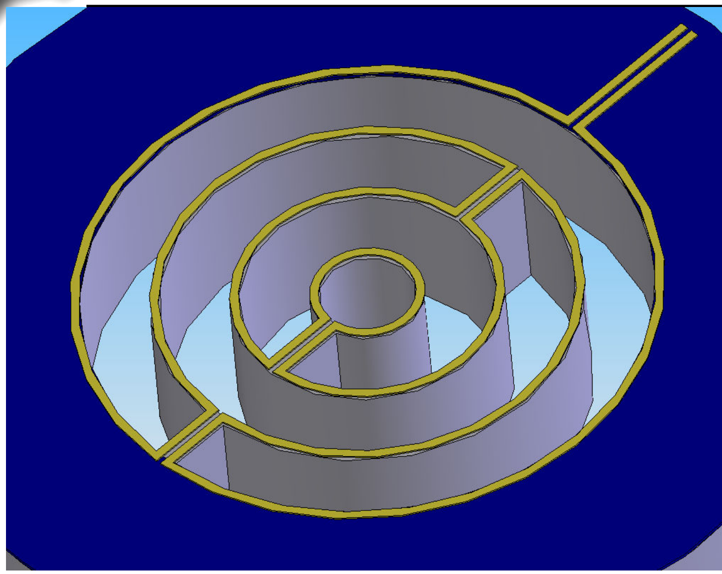
Improved collection performance

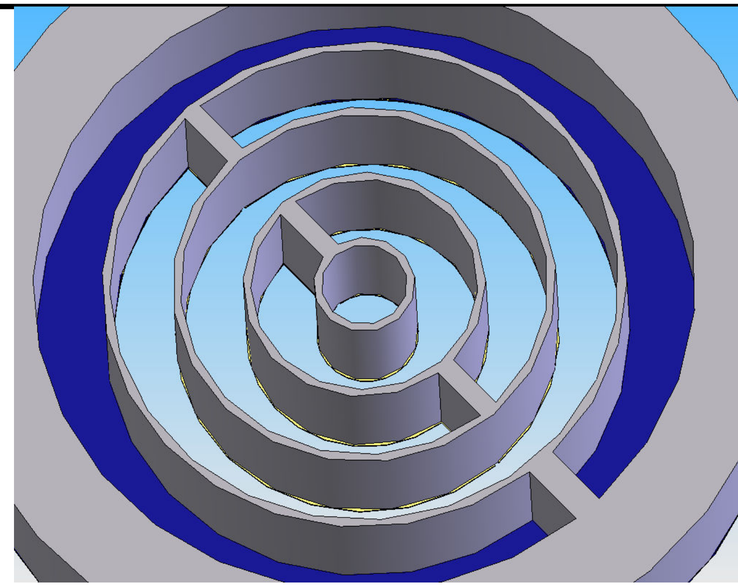
More analytes like volatile organic compounds (VOC)

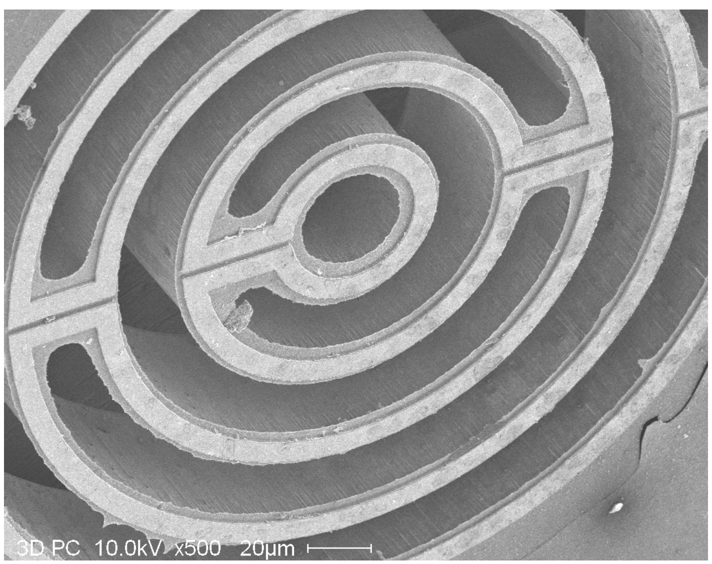


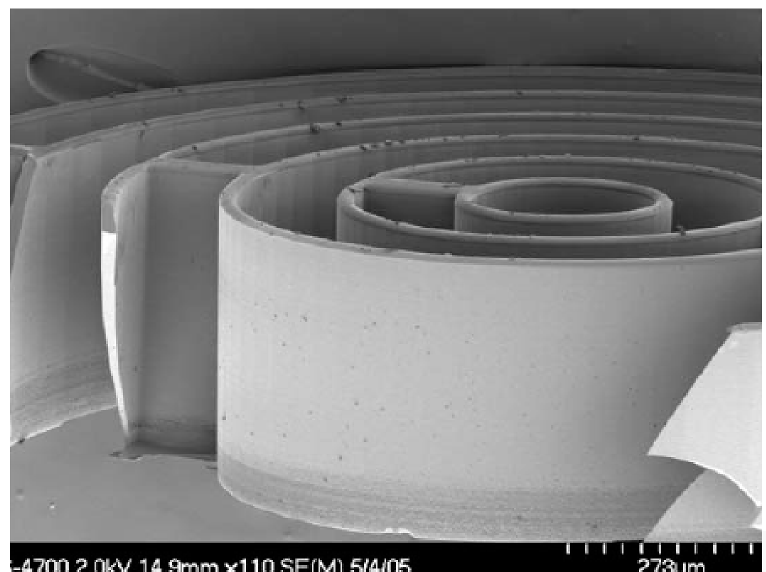


Types of 3DPCs: perpendicular flow. Etching thanks to ITC.









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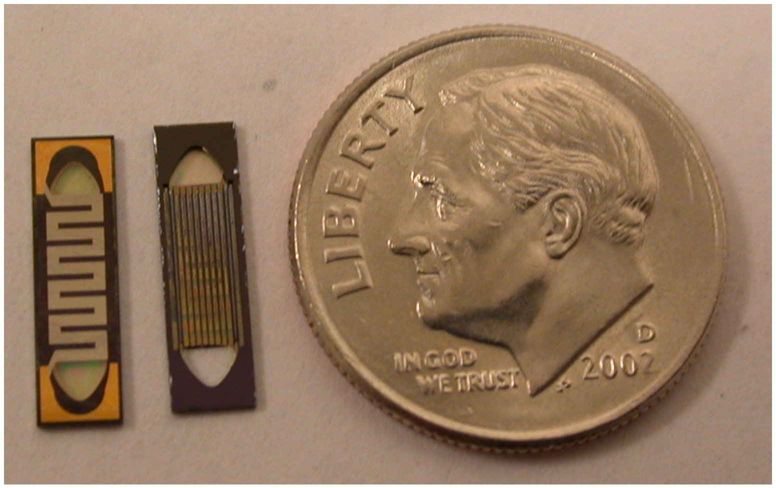
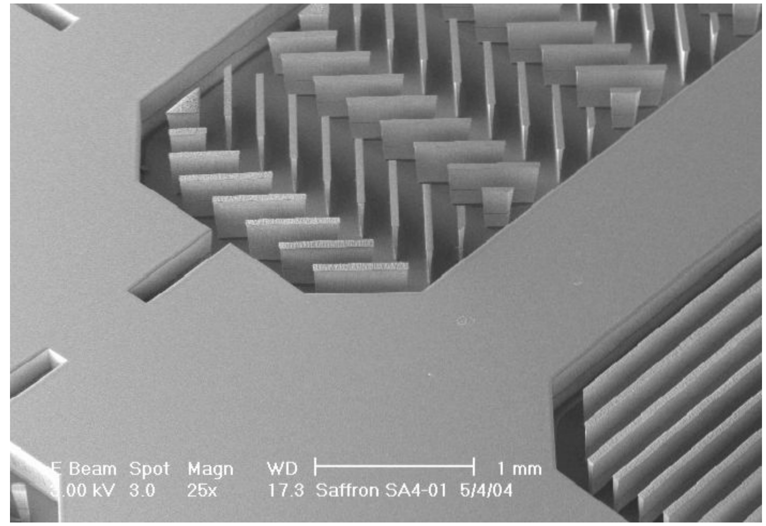
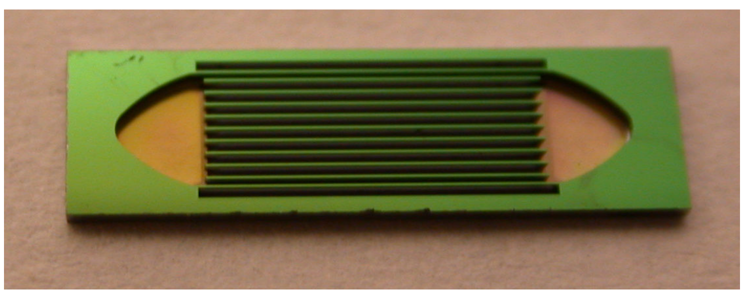
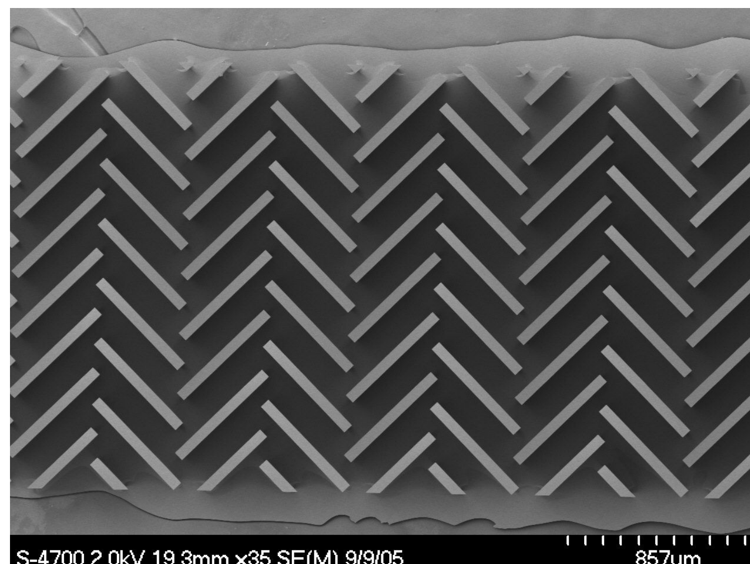
3DPC: parallel flow and tortuous path









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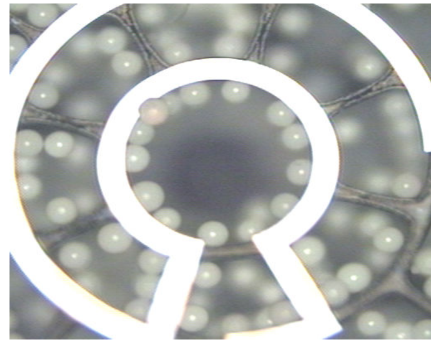
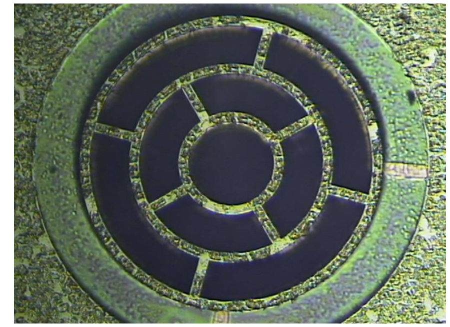
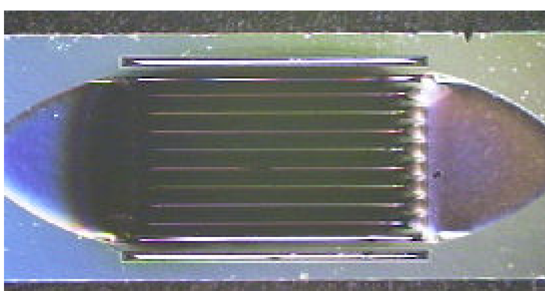
3DPCs, coatings and target analytes: enhanced collection

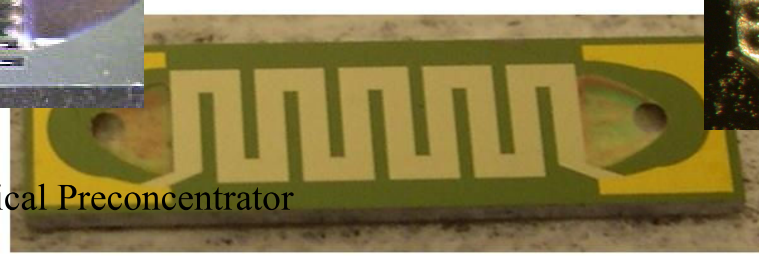
- **Spray and drop coating of sols**
  - CW agents, TICs
  - Explosives – usually need tortuous 3DPC
  - Automated spray with tilt
- **Commercial packing in PDMS binder OR using packing stops**
  - Toxic Industrial Chemicals (TICs) and Tri-Halomethanes (THMs)
  - PoropakQ, HayesepA, Carboxen
- **Laser ablation of nanoporous carbon**
  - Conformal coating; TICs

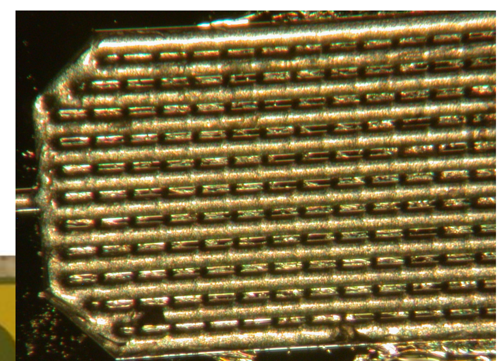




“Perpendicular flow”



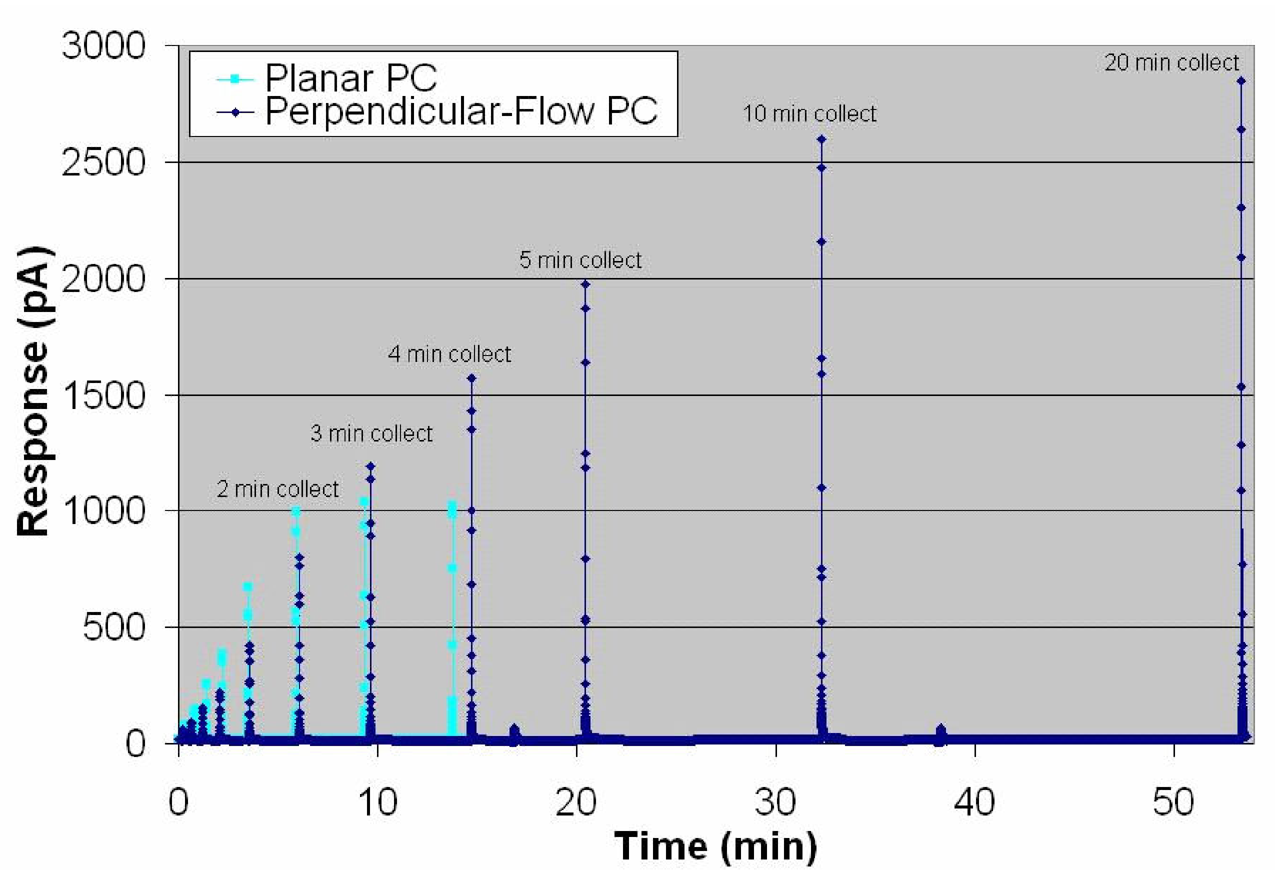


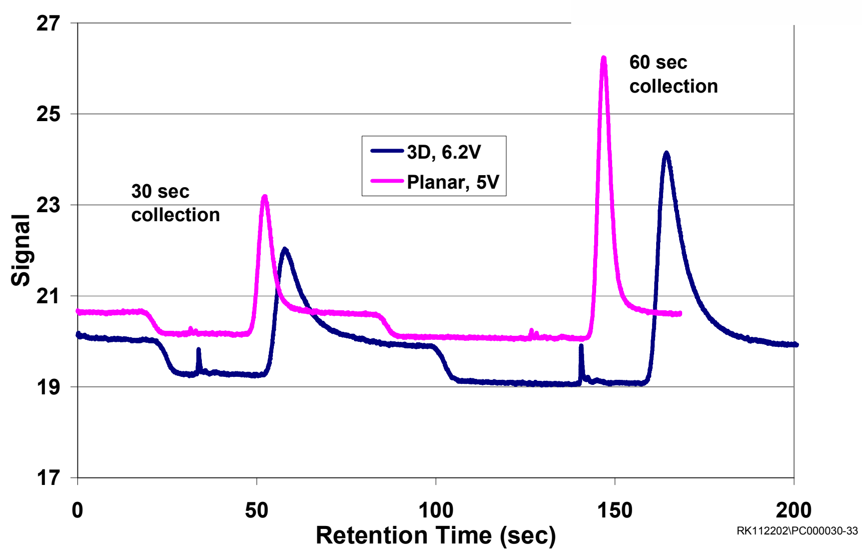


“Parallel flow”

US 7,118,712 Non-Planar Chemical Preconcentrator

3D design aids DMMP collection and release





Thermal uniformity, improved mass transfer

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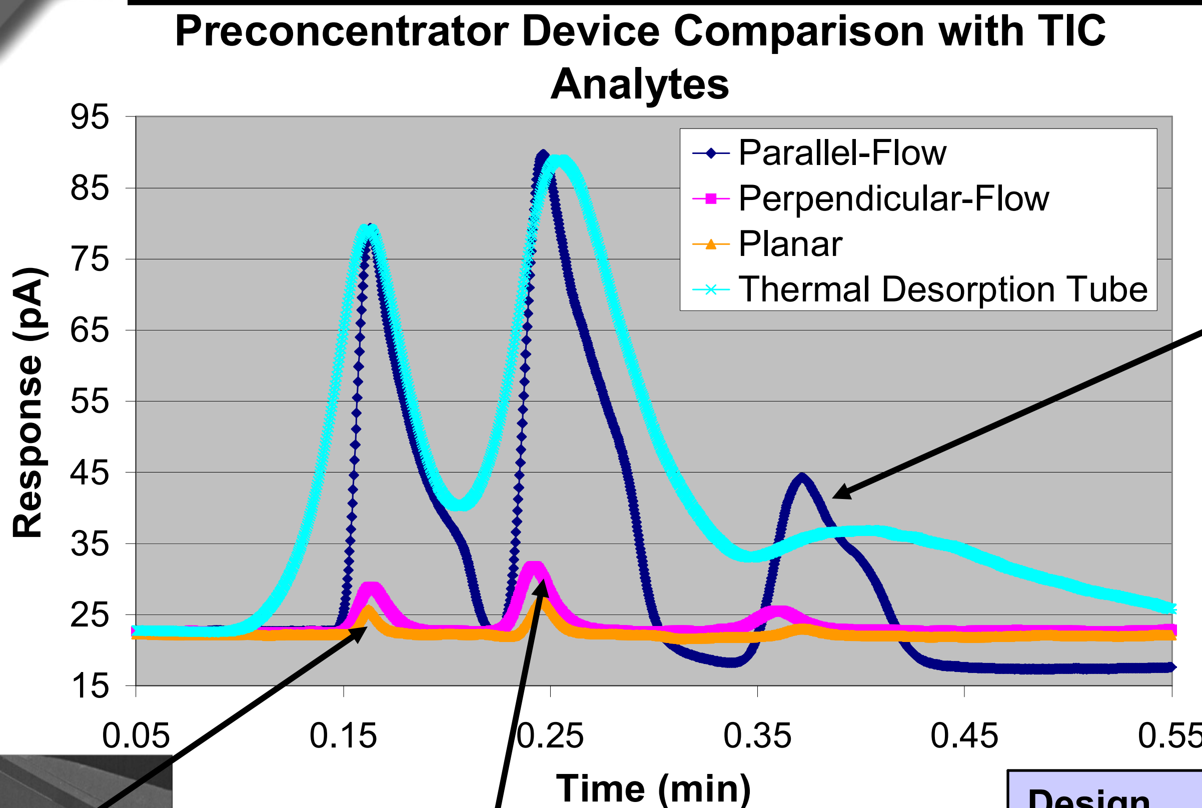
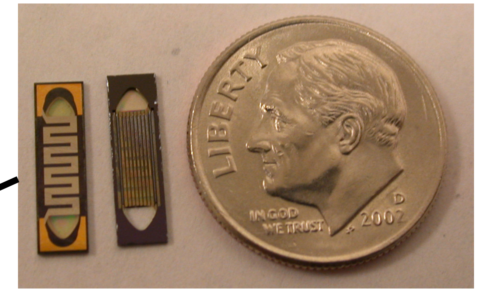
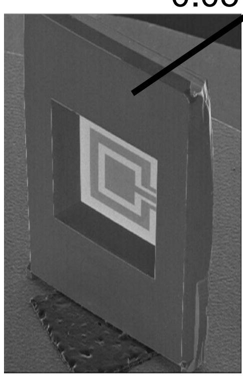
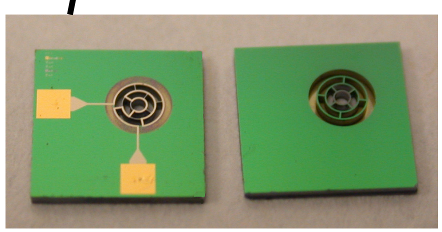
Comparison of Collectors





0.6 W vs 3 W

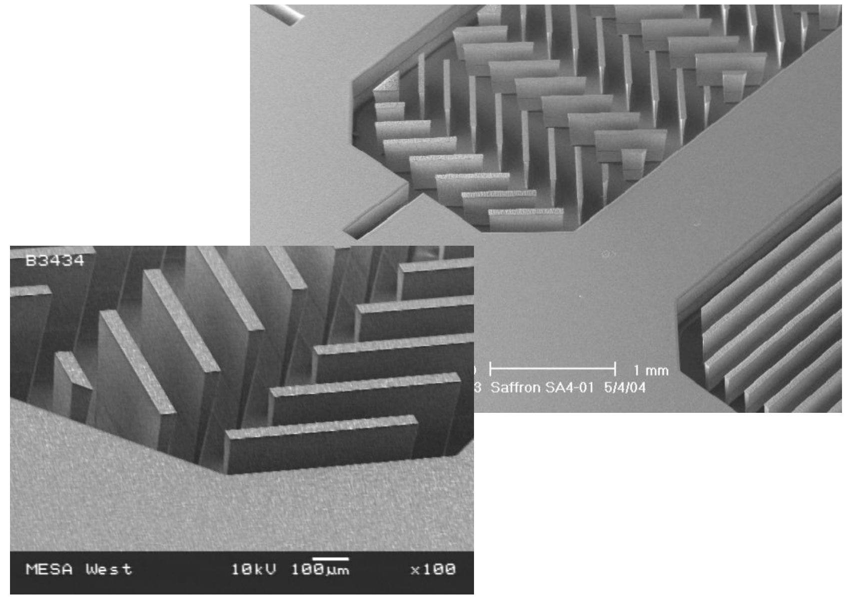


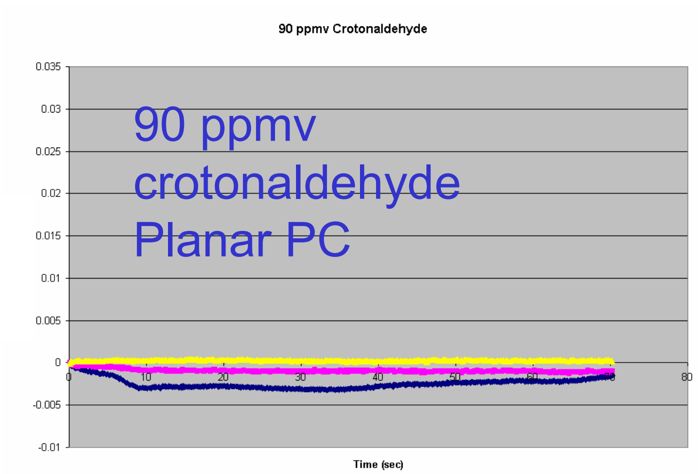


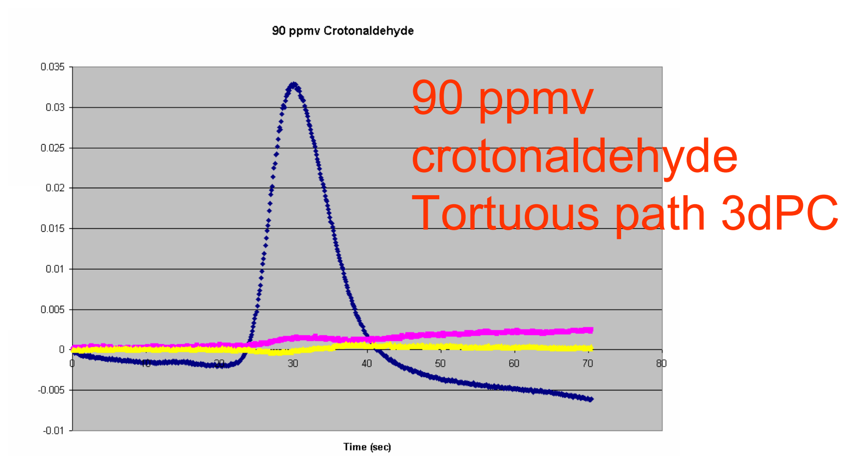
Design	t90 to 200C	Power
Planar	10 msec	100 mW
3D	0.6-1 sec	200-600 mW
Tubular	~minutes	~watts

TIC collection

- Improved collection/desorption – higher surface area, better contact, lower dead volume
- Lower level detection, new analytes
- Ease of assembly
- Water, and VOCs can now be addressed
- TIC, THM, CW
- Explosives







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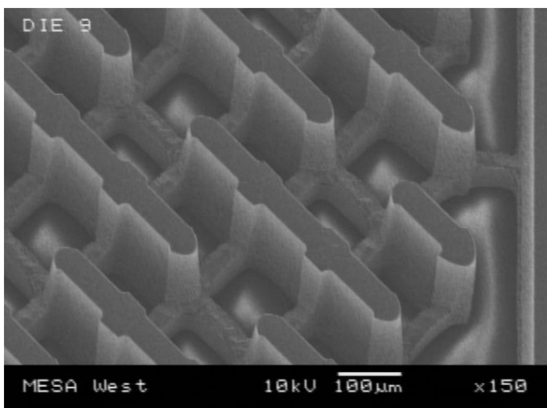
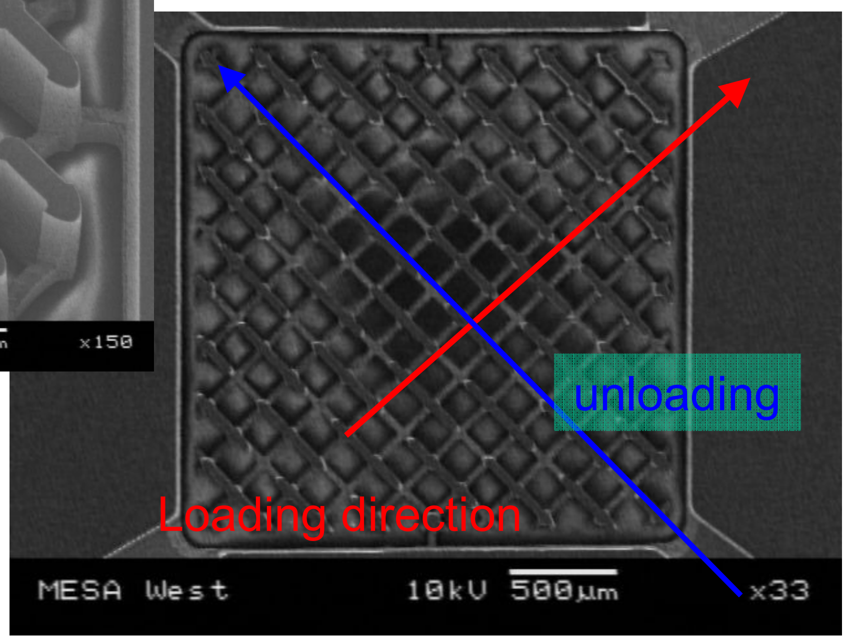
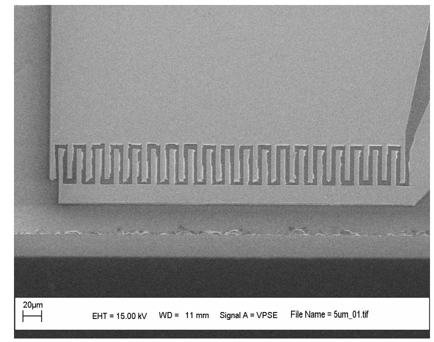
DARPA MGA Requirements

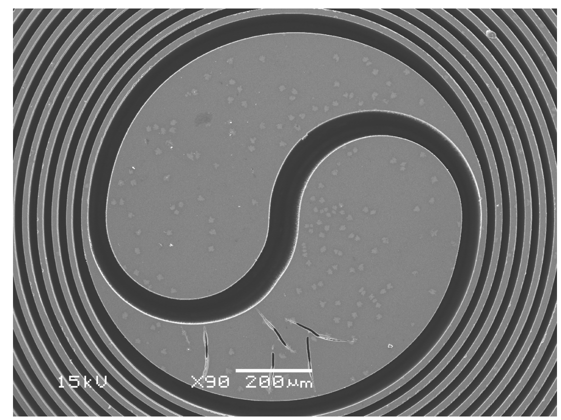
Performance requirements drive enhancements to the system architecture:

Maintain:	Low false alarm rate, <1/200,000
Increase:	Analysis speed, Analytical channel capacity
Decrease:	System volume < 20 cc
	Limit of detection
	Energy consumed per analysis









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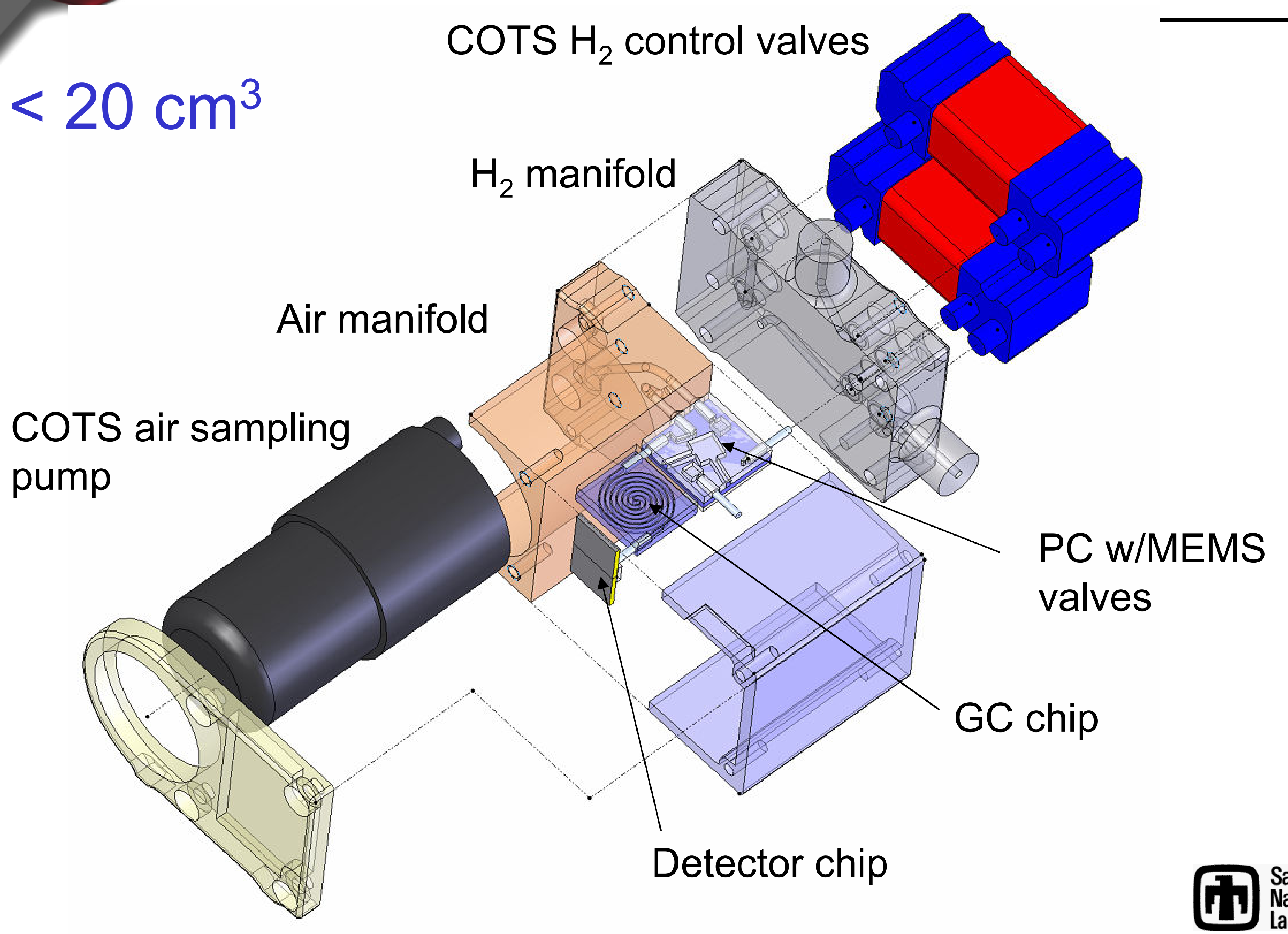
Phase 2 MGA System

< 20 cm³



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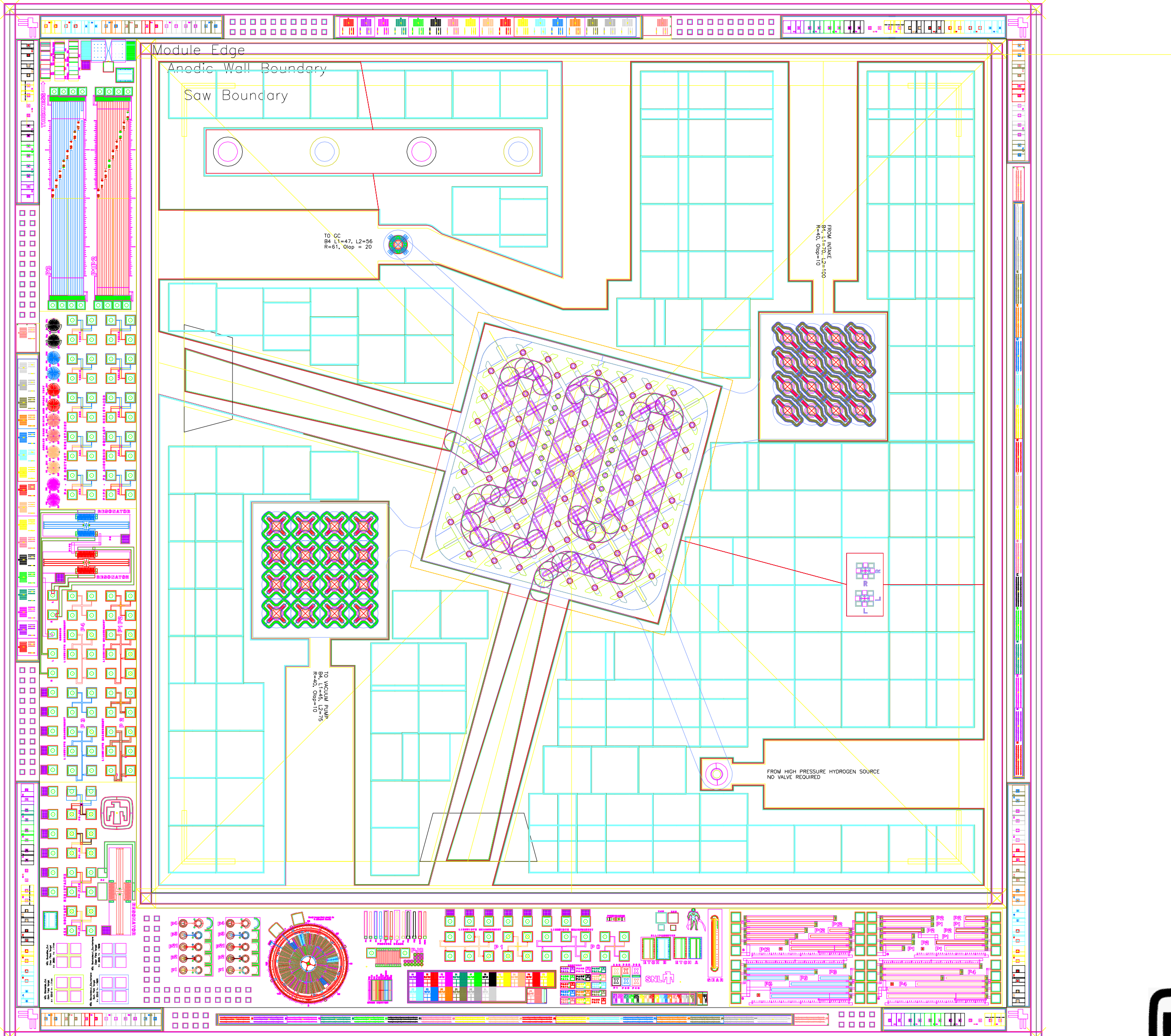
DARPA MGA: MEMS valves on PC chip limit inlet volume



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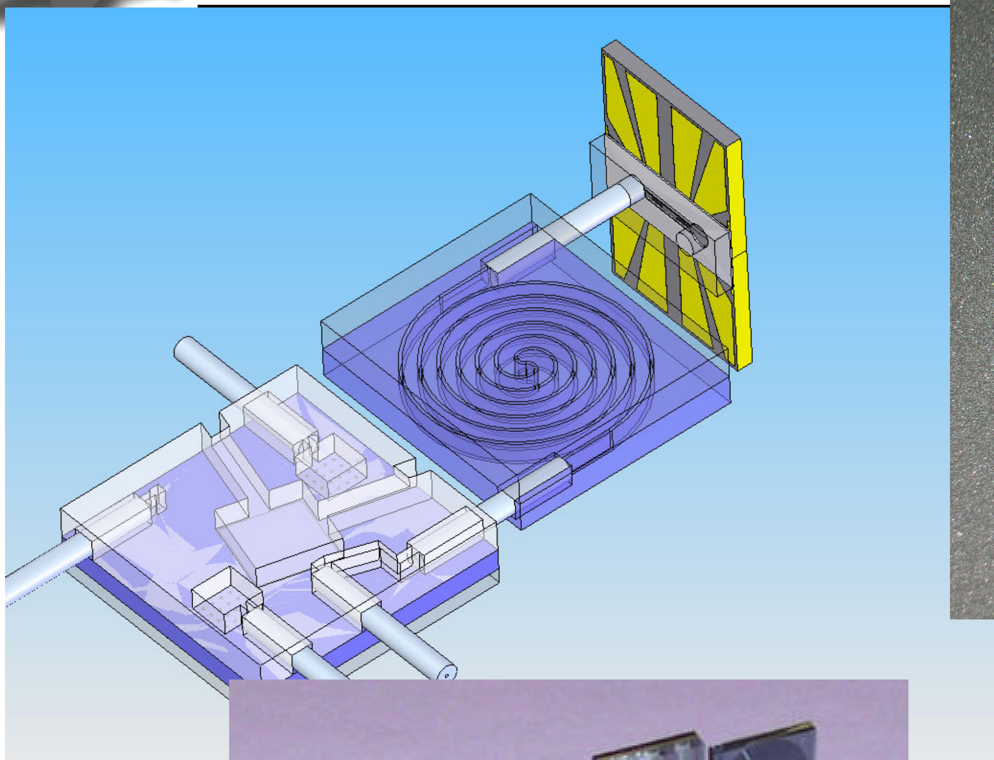
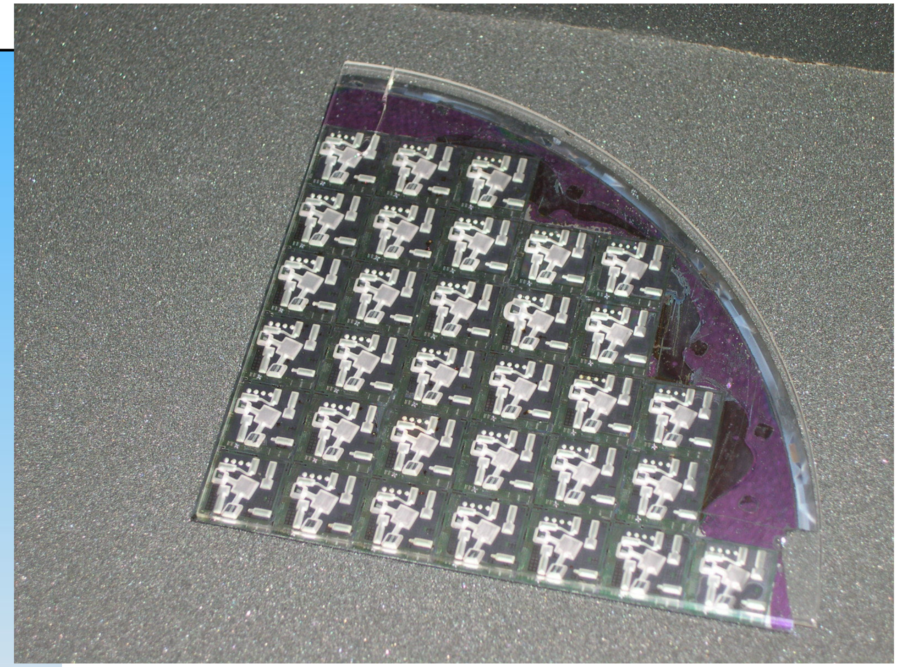
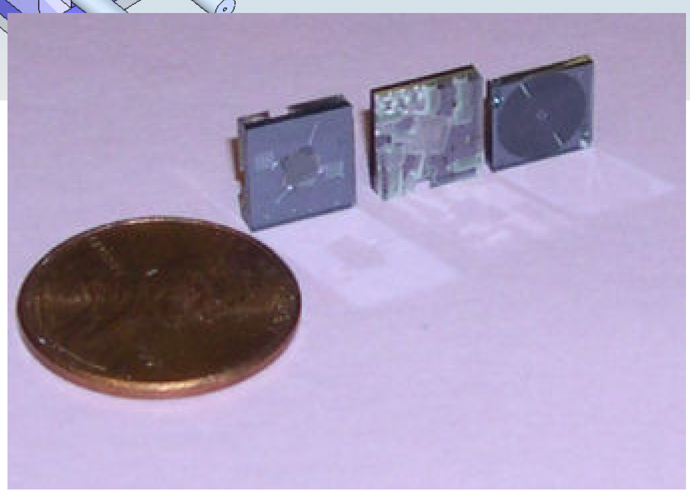
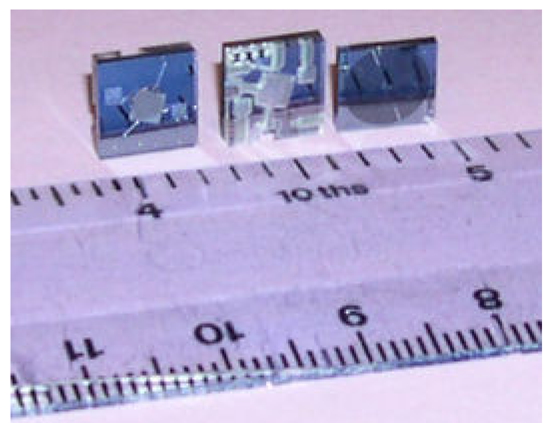
DARPA









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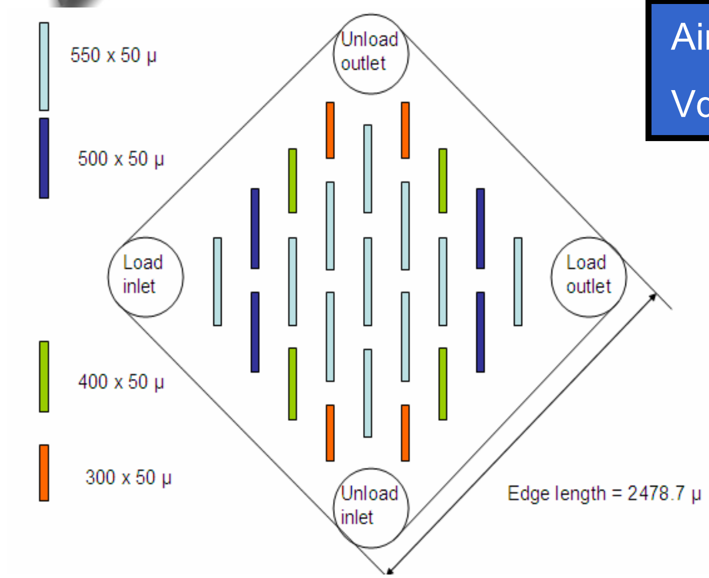
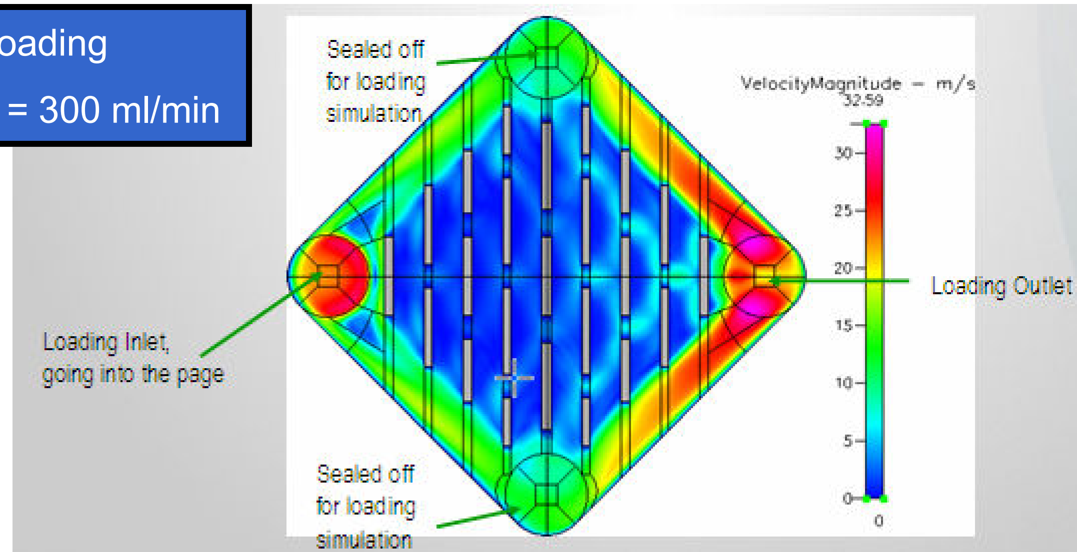
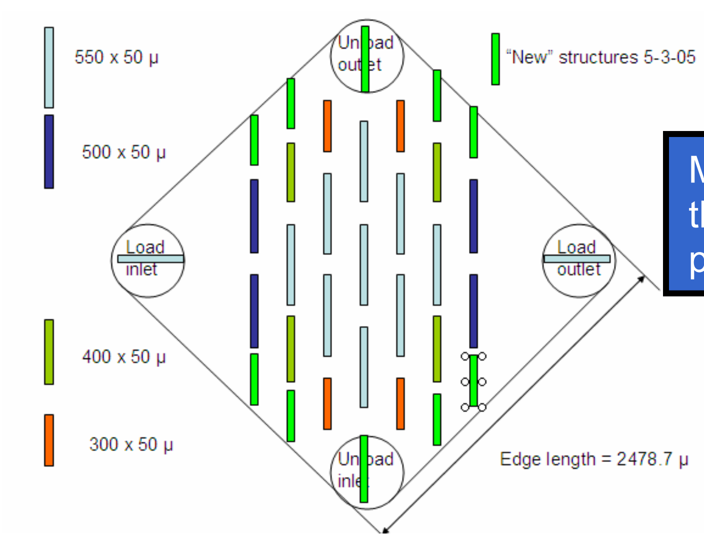
Comparison of Flow Profiles



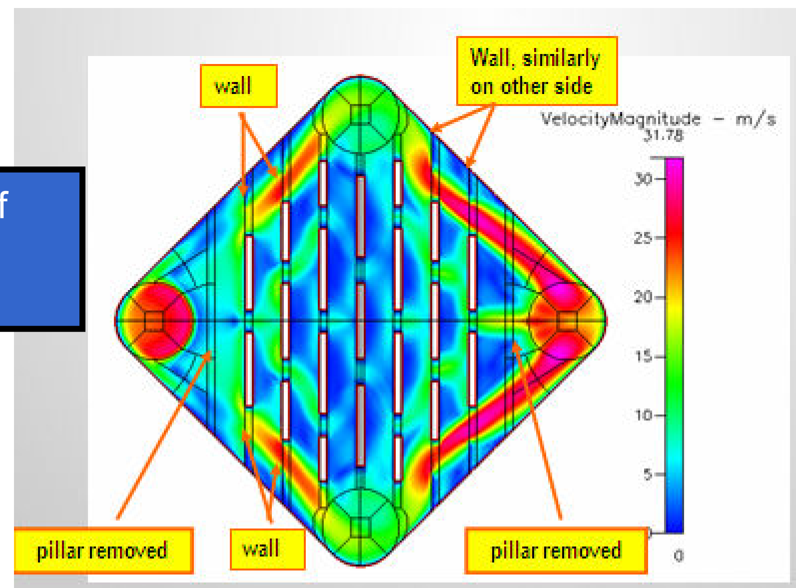
Air Loading

Vdot = 300 ml/min





More wetting of the adsorbent pillars



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Chemistry Simulations

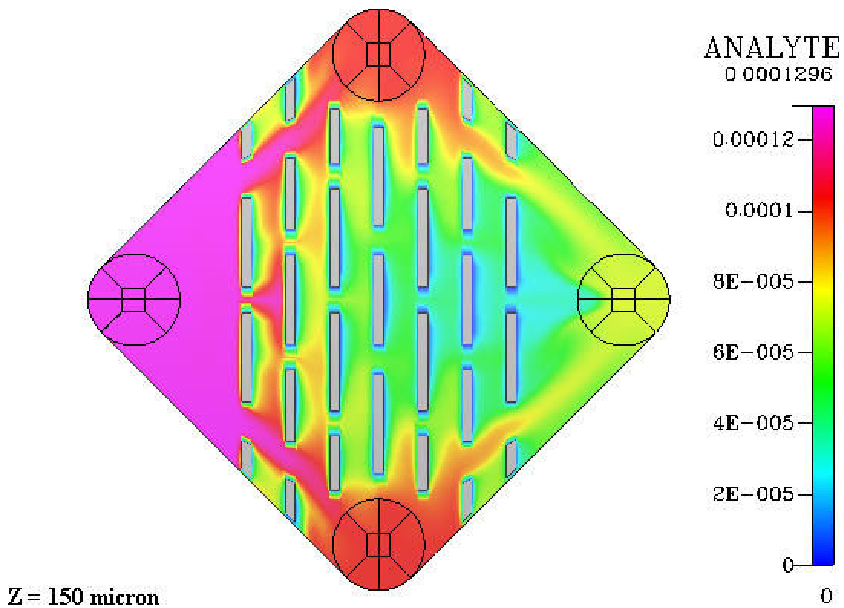
- Once an optimal geometry for flow was determined, four simulations with surface reactions were to be performed
- There are two phases to the chemistry simulations:
  - **Adsorption of the analyte to the surface of the pillars (want the maximum amount of analyte to ‘stick’ and be efficient)**
  - **Desorption and quick evacuation of the analyte from the chip (i.e. narrow distribution of the analyte flux through the outlet)**
- Inlet flow rate and desorption gas were varied
  - **2 different flow rates are used for the adsorption phase**
  - **2 different gases (H_2 and N_2) and 2 different flow rates are used for the desorption phase**

Table of Cases

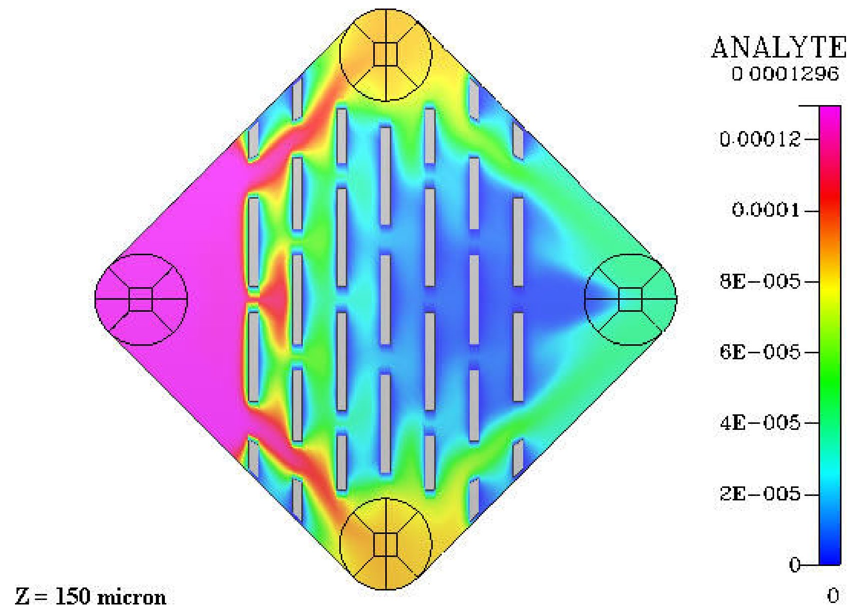
Run #	Adsorption			Desorption		
	Gas	Vdot (ml/min)	Adsorption Time (s)	Gas	Vdot (ml/min)	Desorption Time (ms)
1	**N2**	**60**	**152**	**N2**	**4**	**525**
2	**N2**	**300**	**152**	**N2**	**4**	**525**
3	**N2**	**60**	**152**	**H2**	**6.34**	**525**
4	**N2**	**300**	**152**	**H2**	**6.34**	**525**

Analyte Distribution

Flow Rate = 300 mL/min
Velocity = 23.56 m/s



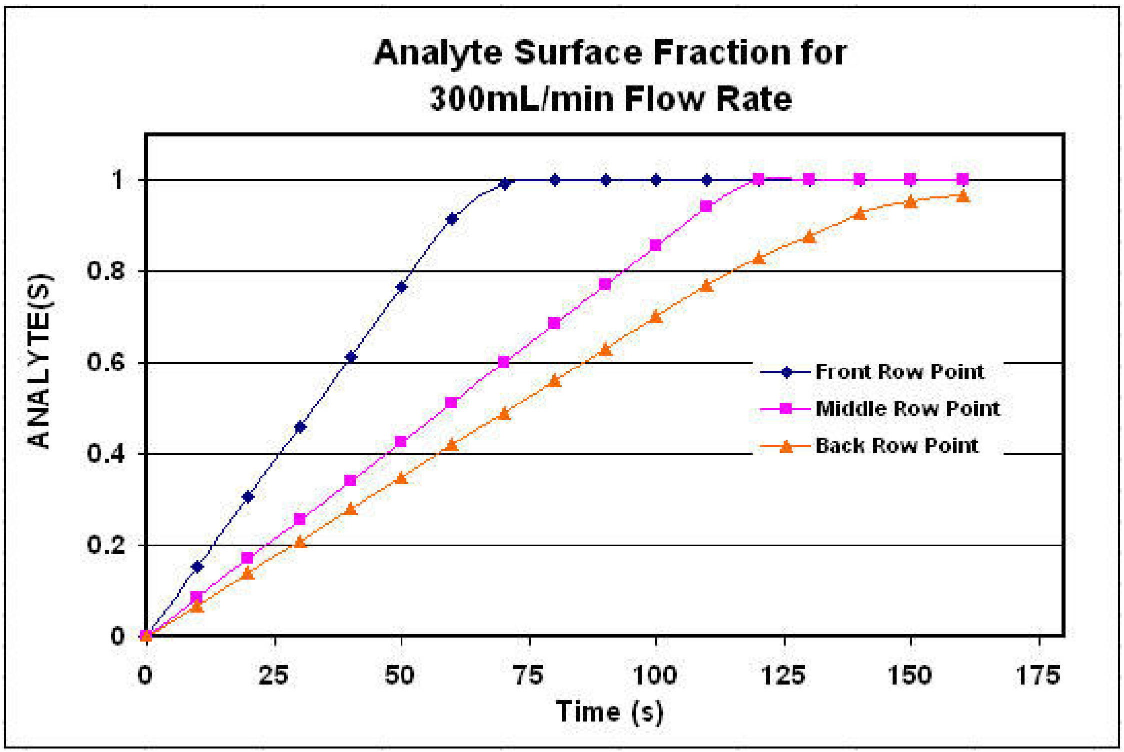
Flow Rate = 60 mL/min
Velocity = 4.711 m/s



- Much more analyte present throughout the chip for the 300mL/min case.
- Analyte concentration drops dramatically across the chip for the 60mL with virtually no analyte on the pillars away from the inlet.

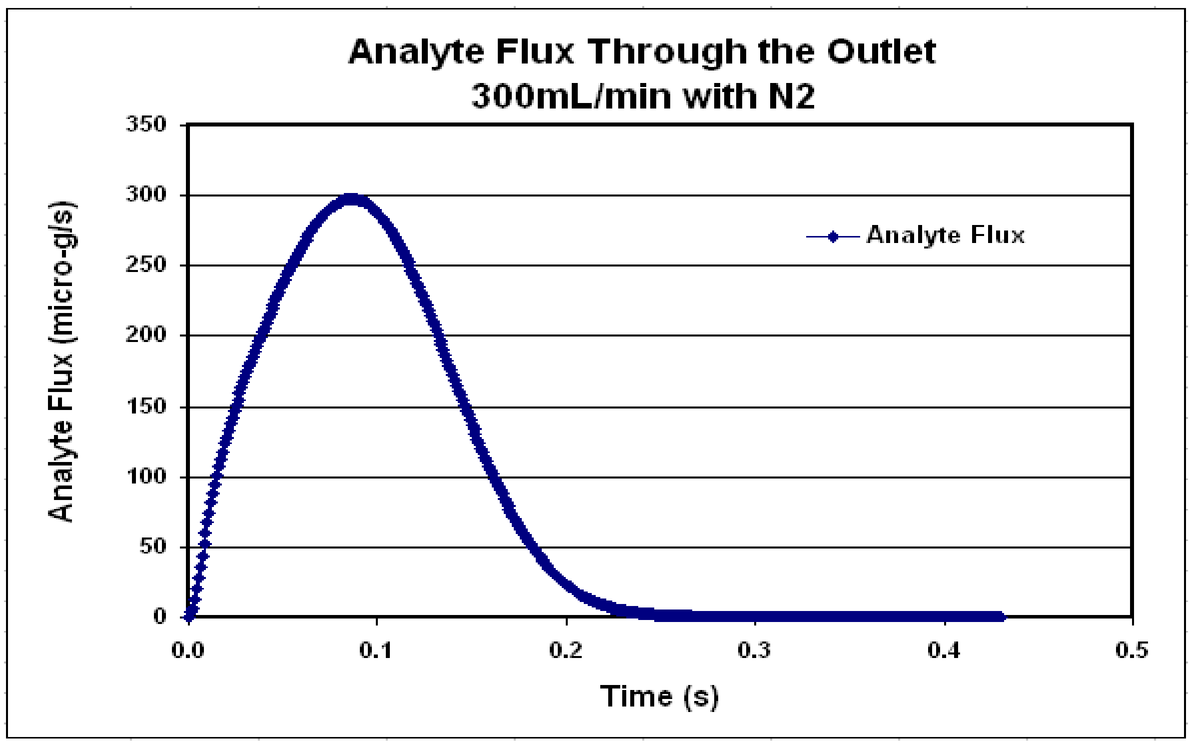
Analyte Site Fraction

- Front row pillars are saturated at ~ 75s
- Middle row of pillars are saturated at ~ 120s
- Last row of pillars are not completely saturated in 152s

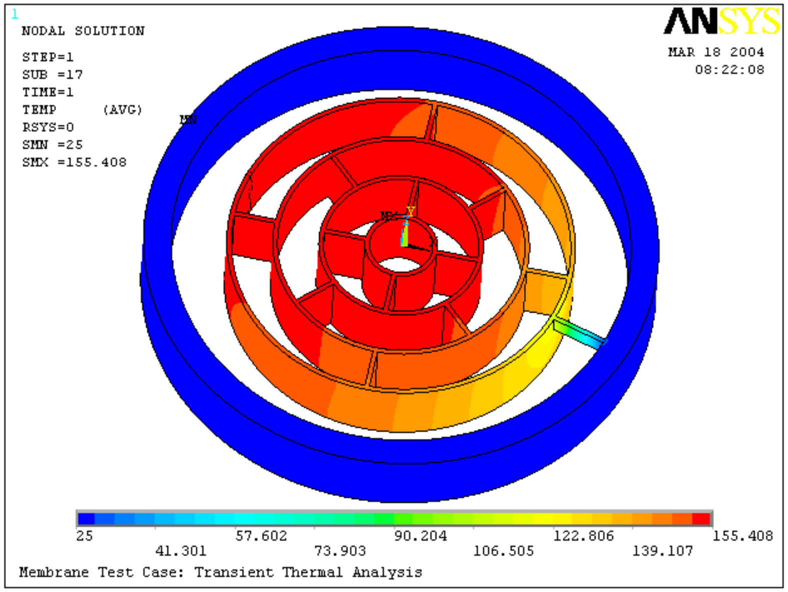


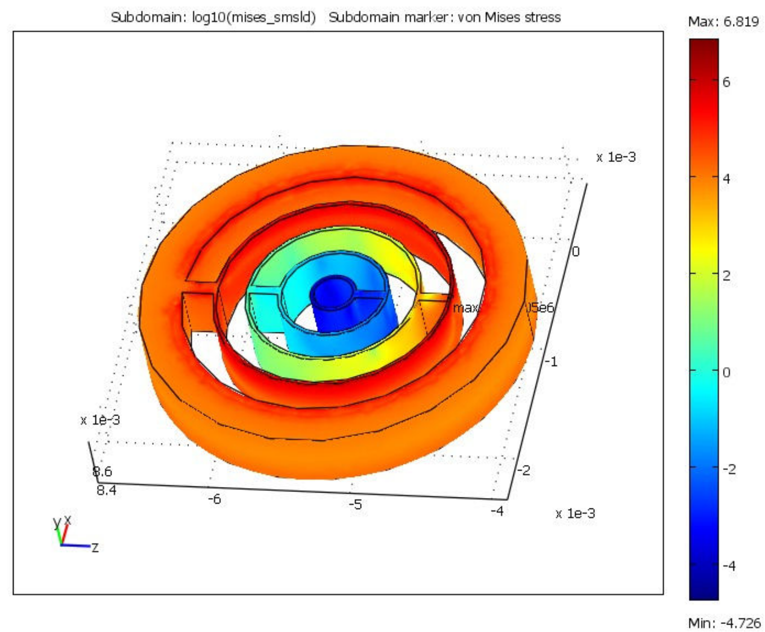
Analyte Flux through the Outlet

- Plot is analyte flux through the outlet
- The maximum flux occurs at 0.09s
- 95% of the analyte has been collected at 0.171s



Other Modeling Efforts





Thermal: Power and desorption speed can be further reduced: 1.3 sec to 0.3 sec to 200ºC

Half wall thickness
Even with a support strut

Mechanical: struts are important

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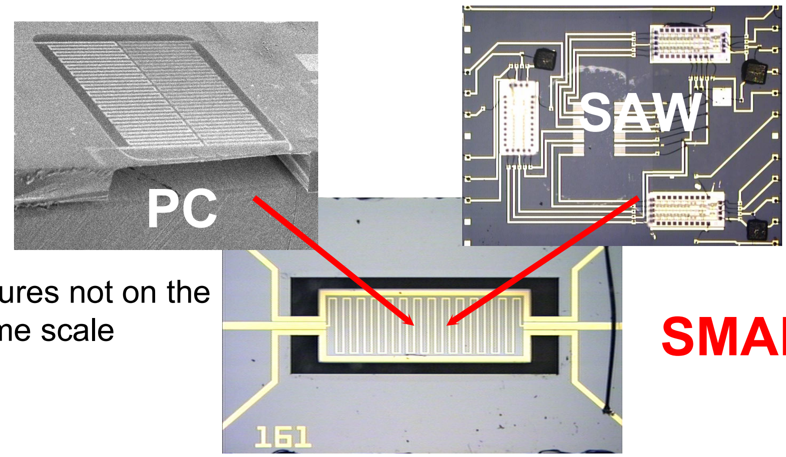
Smart PC™ combines preconcentration and detection to accelerate and automate detection

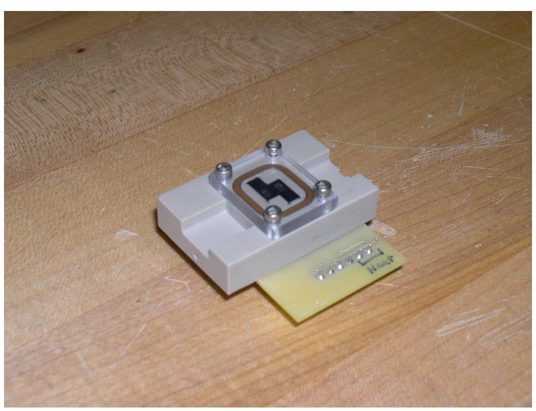
- DOD: reduced analysis times with increasing target concentration
- MEMS resonator with a heater/adsorbent weighs the sample & decides when it has collected enough
- Modular fixtures
- Circuit autotunes, autozeros
- Software subtract reference and smooth

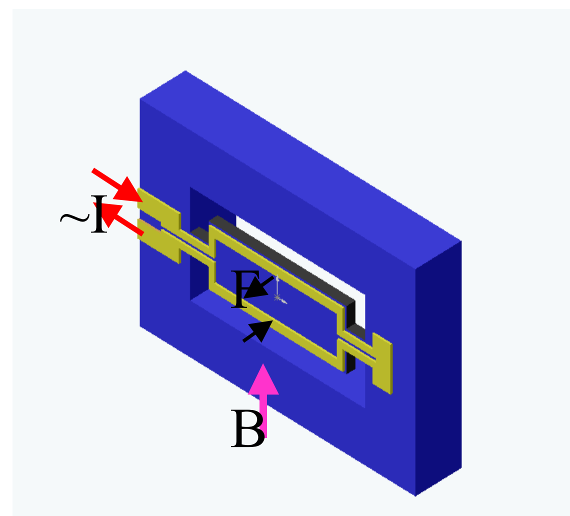


Figures not on the same scale

SMART PC™

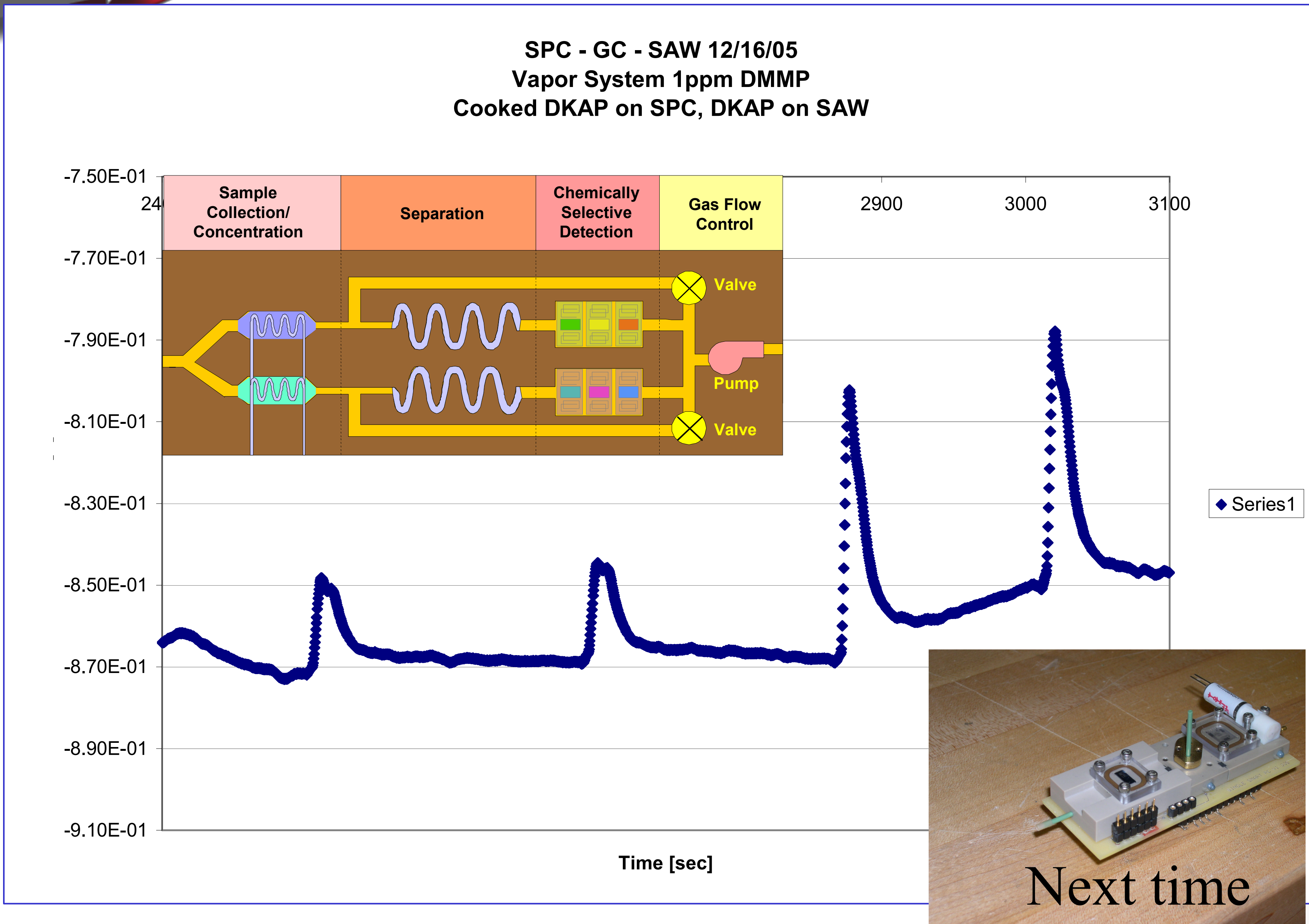
Reduced need for trained operators



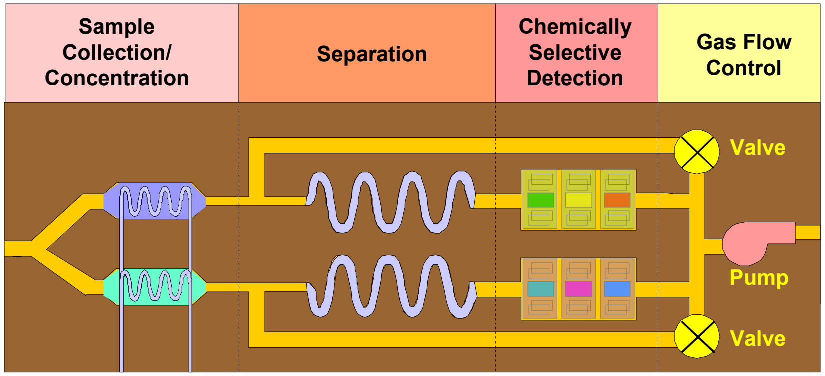


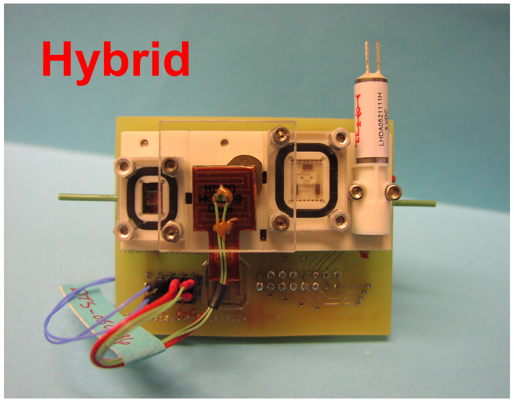
USPTO 7,168,298 Mass Sensitive Preconcentrator

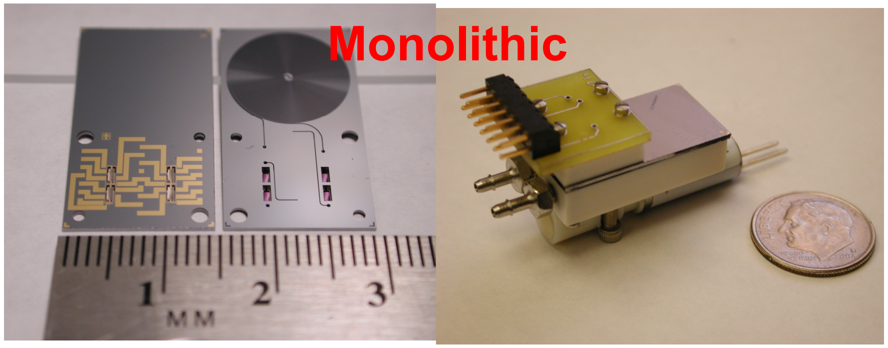
Detection with selectivity: 7 times faster at LC50 of Sarin



The microchemlab uses preconcentration, separation and selective detection to perform real-world analysis: hybrid or monolithic packaging plays an important role







+ Modular adaptability
- Unheated transfer
- Long transfer
- Relatively larger
+ Reduced thermal isolation concerns

+ Lowest dead volume – best performance
+ Heated, short transfer
+ Short transfer
+ Relatively smaller
- Thermal isolation issues – solved by ramping
+GCs tested with CW simulants

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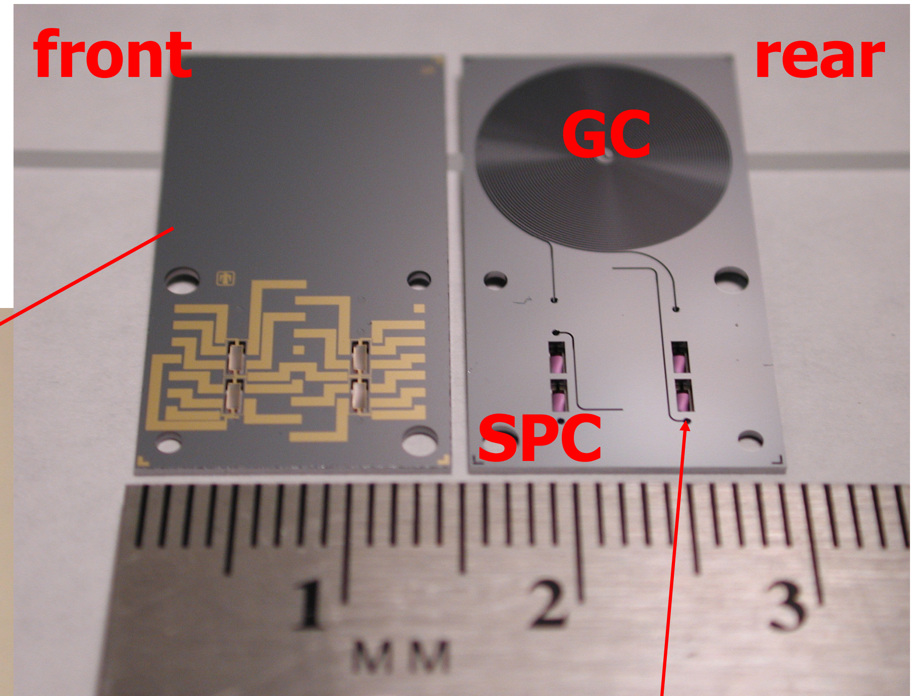
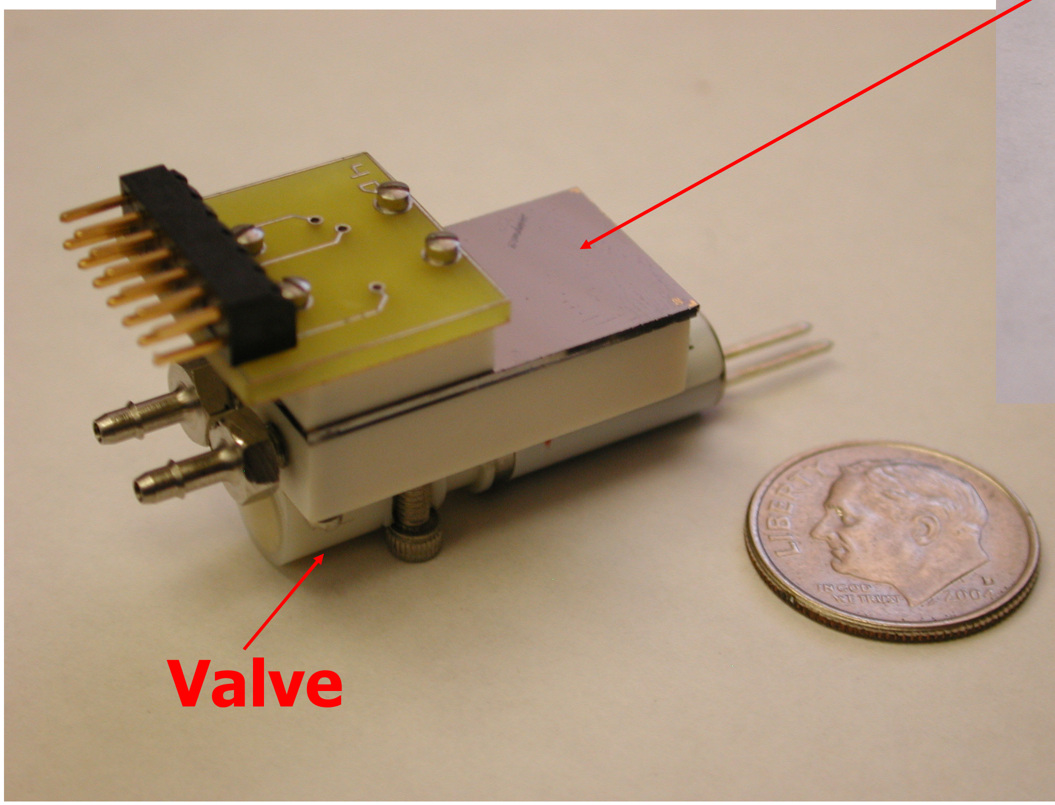
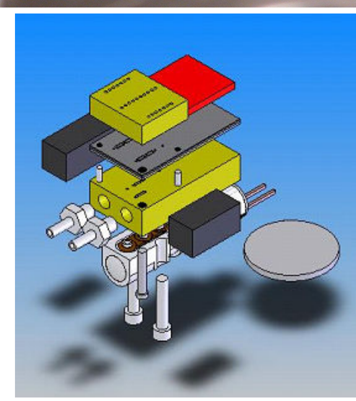
Integrated System for reduced dead volume, size, cost, etc.

- Smallest MicroChemlab Yet
- Coatings, GCs demonstrated

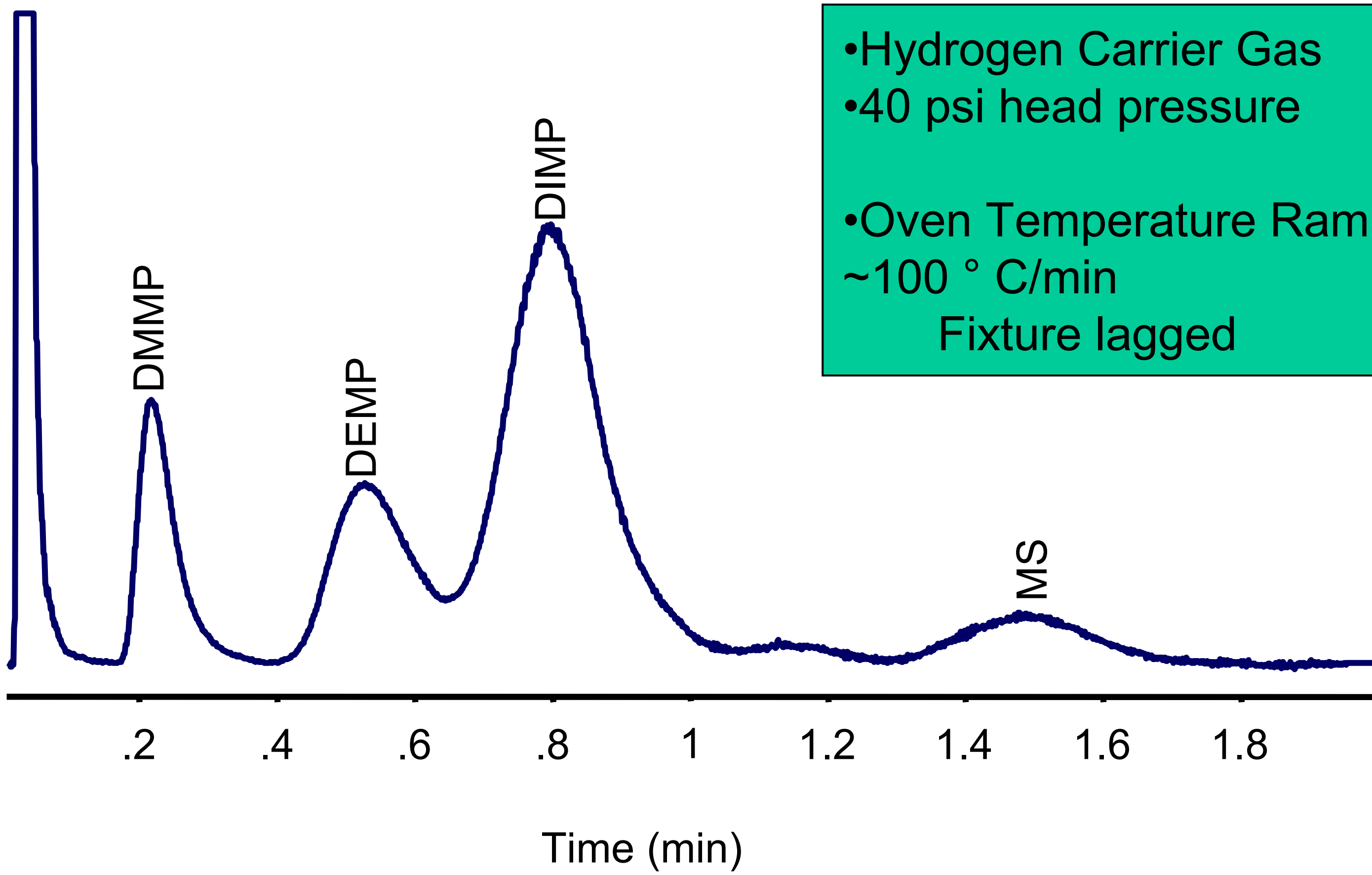






SPC Detectors

Monolithic GC Operation



- Hydrogen Carrier Gas
- 40 psi head pressure

- Oven Temperature Ramp
~100 ° C/min
    Fixture lagged

Acknowledgments

- Thanks to GOSPEL Workshop Organizers
- DARPA MGA, Dennis Polla
- Sandia Labs LDRD Office
- Dr. Elizabeth George and Dr. Randy Long, DHS

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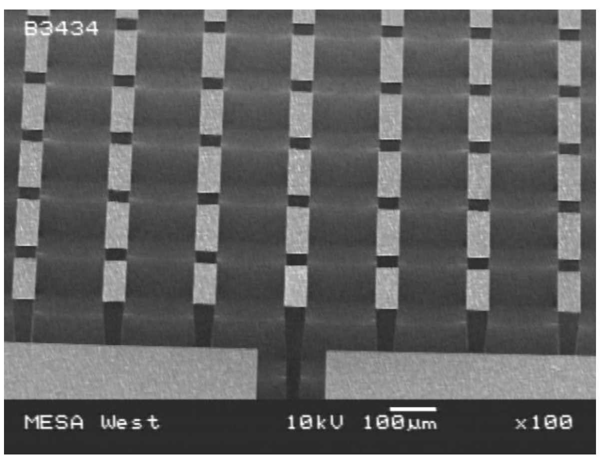
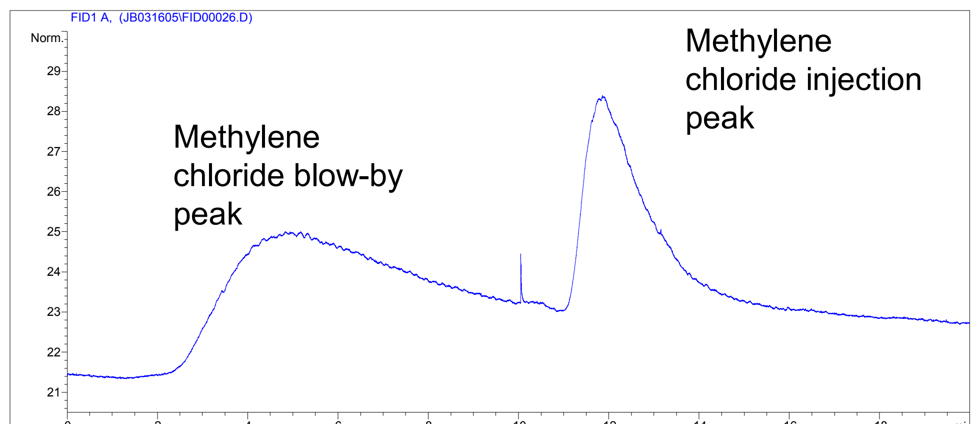
Extras Follow

Tortuous Path Base-Catalyzed Sol-Gel Excessively Coated Preconcentrator Collection Efficiency for Various Analytes

Analyte	Mass Injected (ng)	Area of Blow-by Peak	Area of Injection Peak	*% efficiency	Vapor Pressure (mmHg @ 25 C)
Methylene Chloride	**1657**	**2092**	**523**	**20**	**435**
Chloroform	**910**	**334**	**538**	**62**	**197**
Hexane	**613**	**926**	**3584**	**79**	**151**
Heptane	**236**	**11**	**1799**	**99**	**46**

One of the Lower Tortuosity Designs





*** % efficiency = Area injected/ (Area blow-by+ Area injected) x100**

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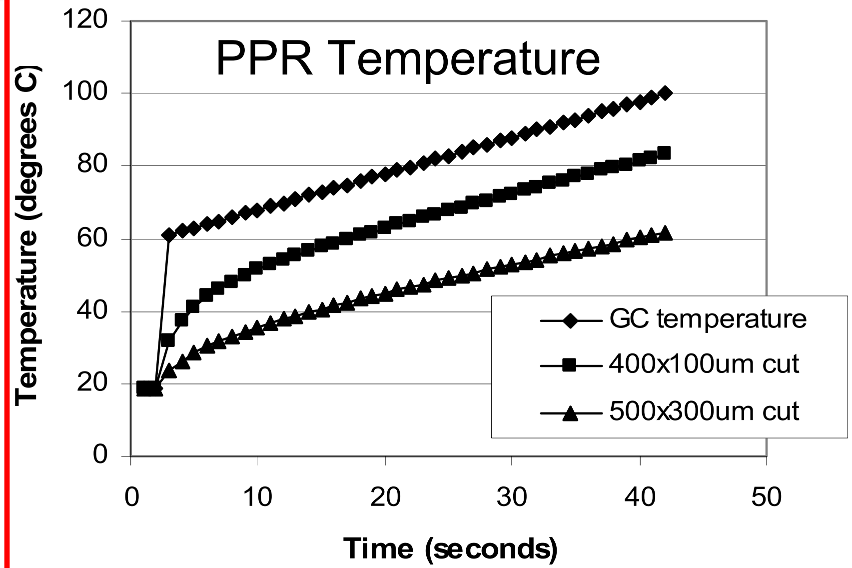
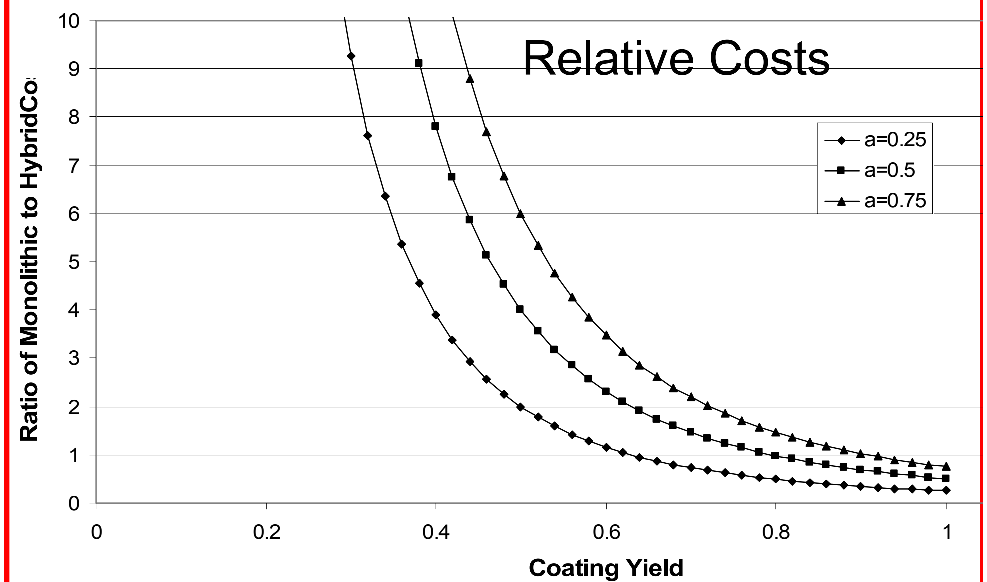
The benefits of monolithic integration can be realized while mitigating concerns for thermal cross talk and cost

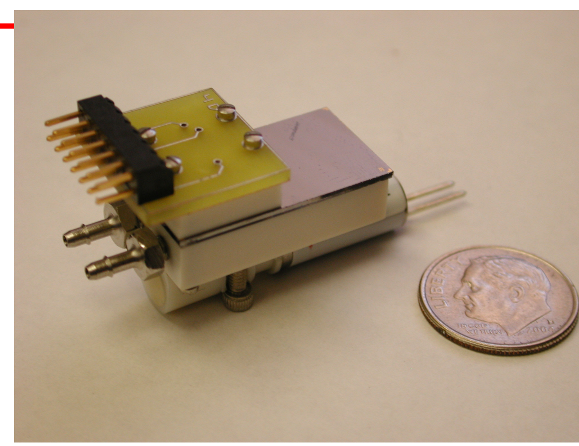


GC temperature ramping and isolation techniques allow monolithic



Improved coating yields make the monolithic system more cost effective than modular

Progress:
Smallest microchemlab yet
Coatings and GC demonstrated
Complete testing soon
Die yield at 63%; No flow leaks
Paper submitted to IEEE Sensors Journal



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