SAND2007-0927C

Development of a High-Speed High-Performance Microfabricated Gas Chromatograph

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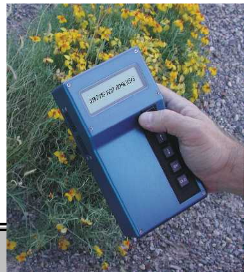
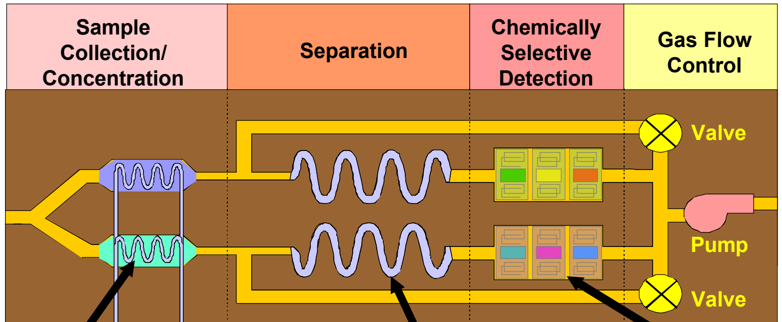
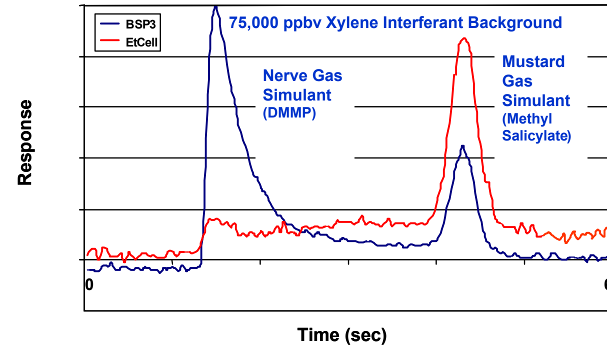
μChemLab™ at Sandia National Laboratories

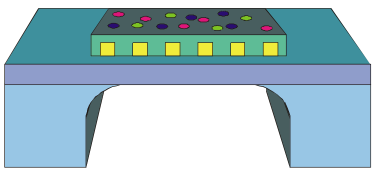
Hand-held chemical analysis system that uses three microfabricated stages.

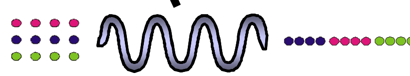


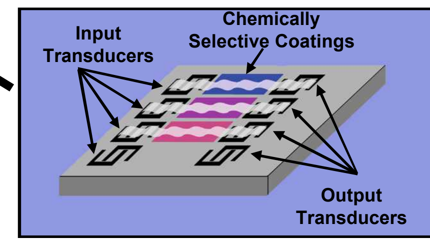
- 8”x4”x2”
- 2 min. analysis
- 4W max. power







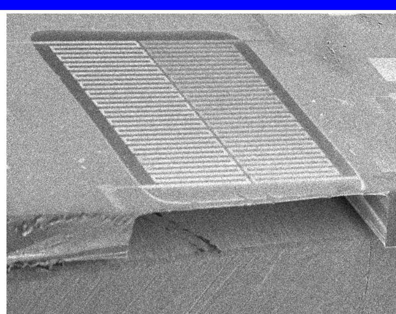


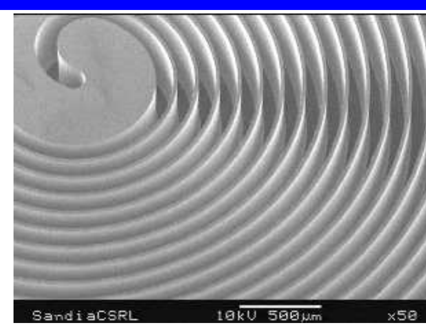


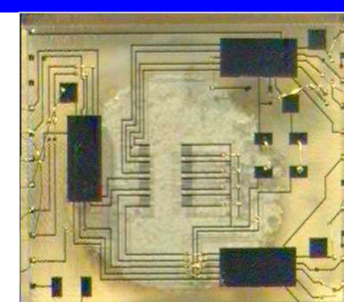
Preconcentrator accumulates species of interest

Gas Chromatograph separates species in time

Acoustic Sensors provide sensitive detection







Over a decade of development in small, low power, selective gas chromatographs.

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Next Generation Development

Program Goals:

High Speed, **High Performance** GC

- Size
  - Small Size
    - **<20cm^3 Total Volume**
  - MEMS Integrated Components
- Speed
  - High Speed Separations
    - **8 components separated from 8 interferents in 4s**
  - Hydrogen Carrier Gas
- Power
  - Low Power
    - **<3J/analysis**
  - Catalytic Combustion of hydrogen for heating column
- Resolution
  - High Performance
    - **Total Analytical Peak Capacity >100 in 4s**
  - High Aspect Ratio MEMS (HARM) columns

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Modeling Predicts *System* Efficiency Using Rectangular GC Columns

1st 3 terms model column performance, 4th term connects column to system

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

$\bar{u}$ – 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

L – column length

Δt – time correlating to extra column band broadening

$$\Delta t = \frac{\text{inlet (or outlet) volume, cm}^3}{\text{gas flow rate, cm}^3\text{/sec}}$$

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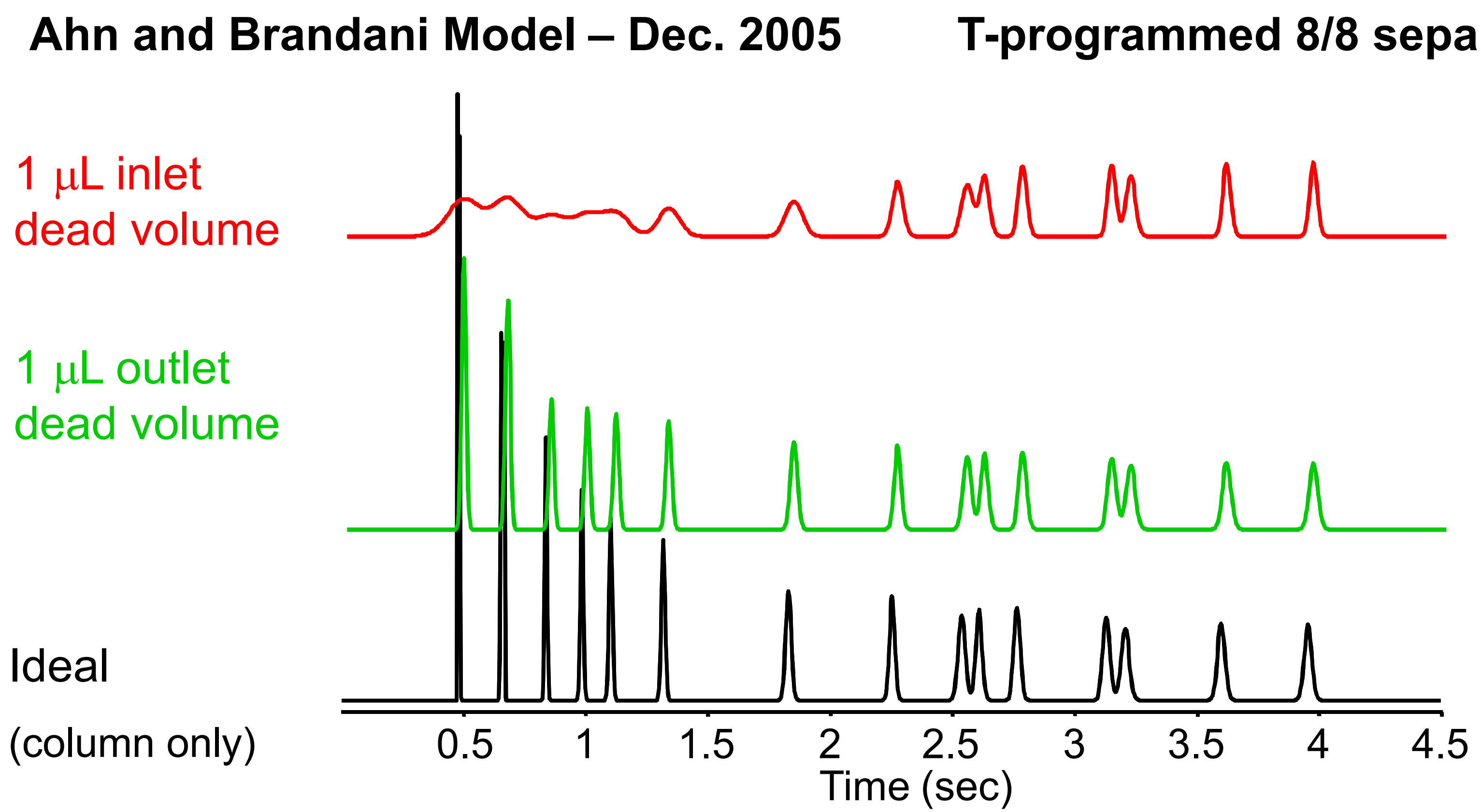
Integration Driver: Modeled GC Band Broadening



Inlet dead volume costs more than outlet dead volume due to carrier gas compressibility: $(cm^3/sec)_{outlet} > (cm^3/sec)_{inlet}$

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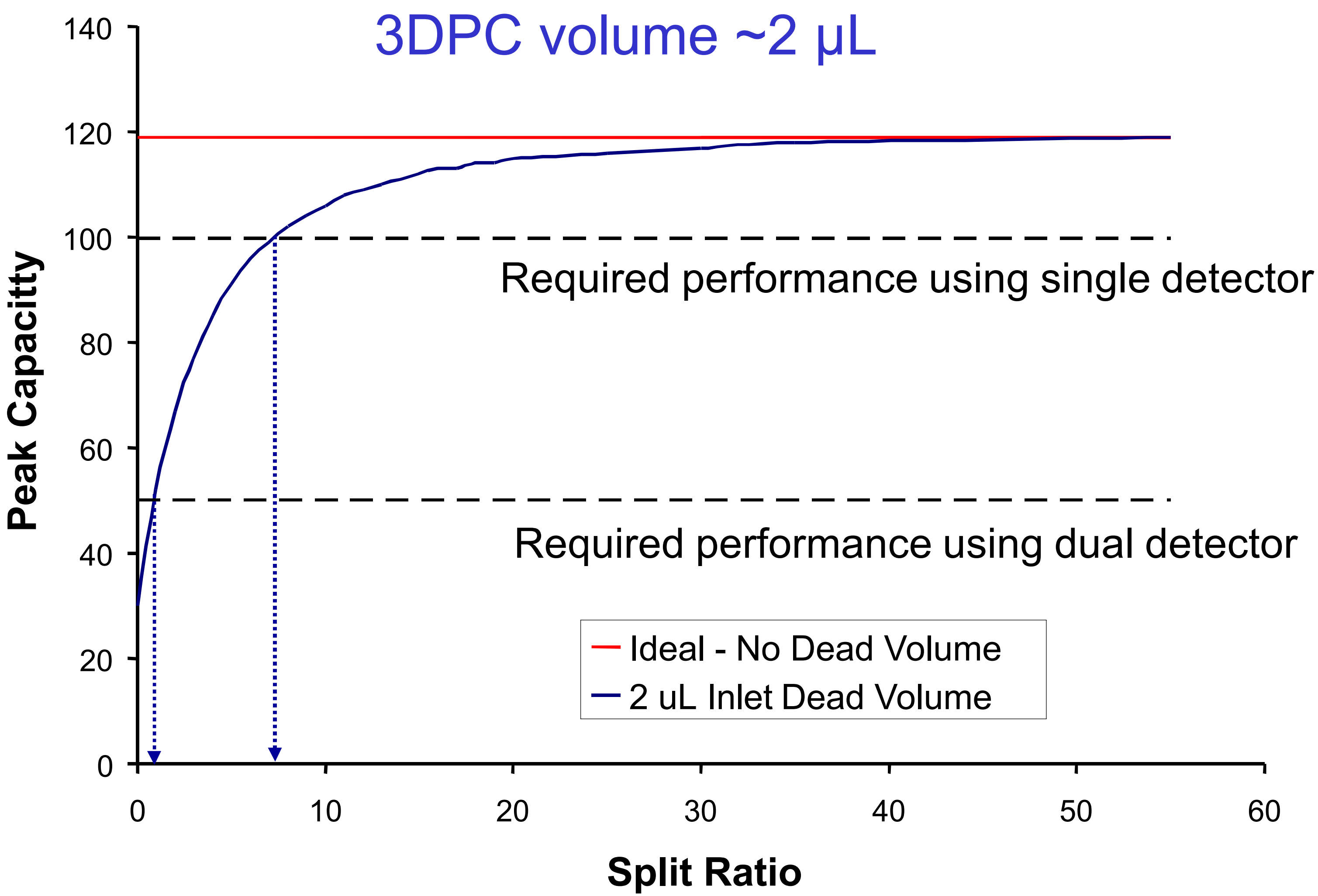
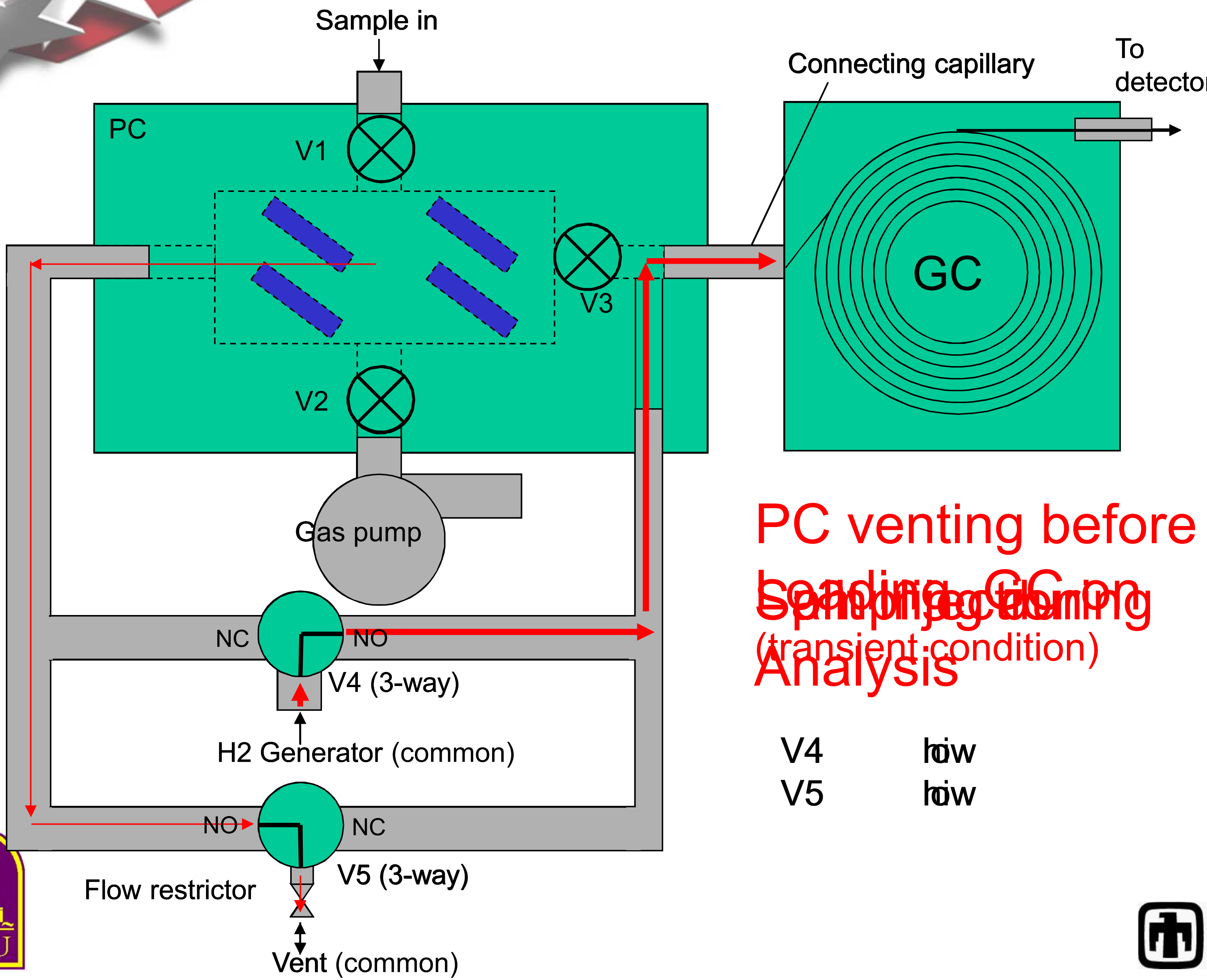
Mitigating the Effects of Inlet Dead Volume
GC Peak Capacity vs. Injection Split Ratio



2 External Valve System Schematic



PC venting before Loading GC on

Sampling / Injection / during

(transient condition)

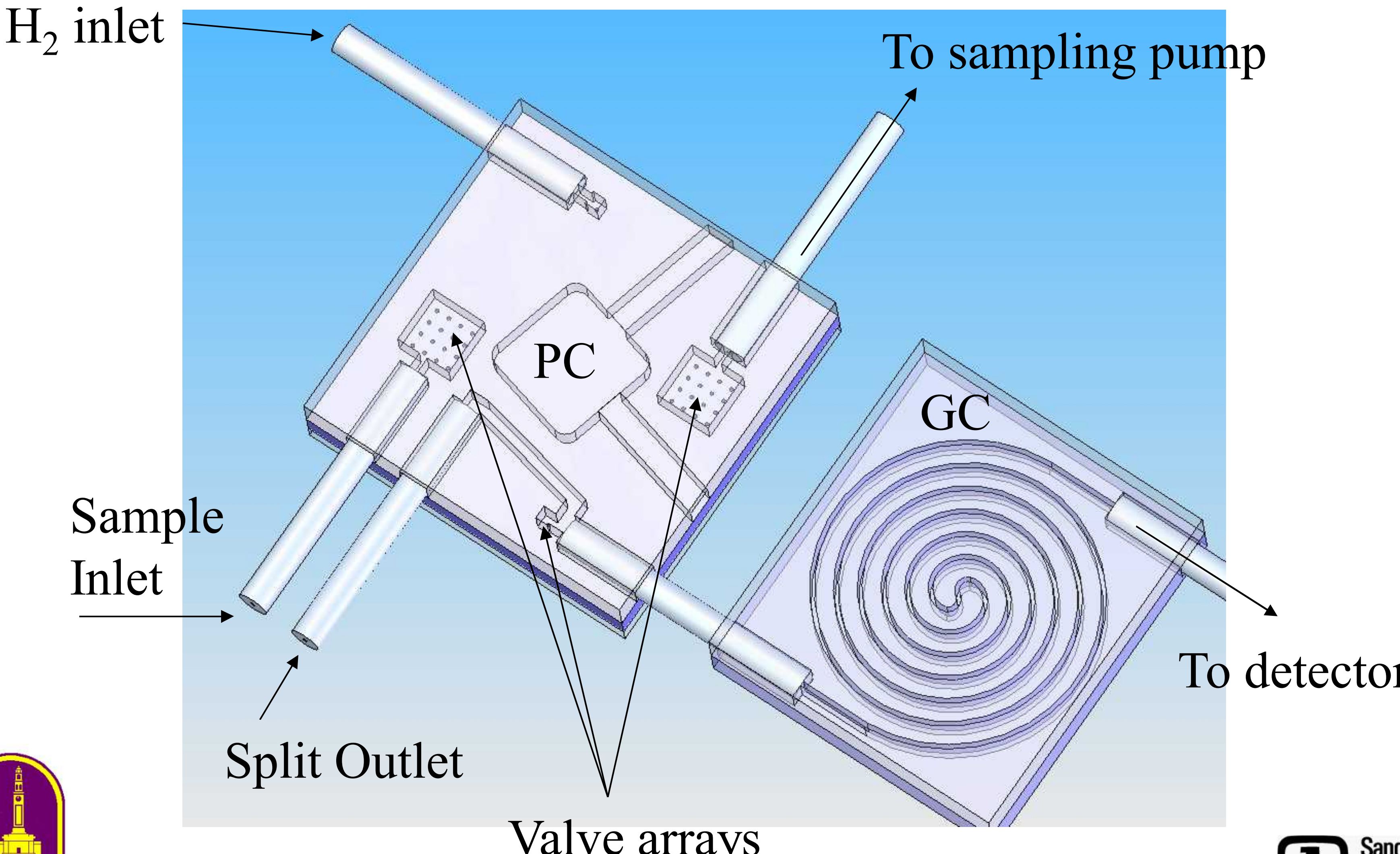
Analysis

V4 hi / low

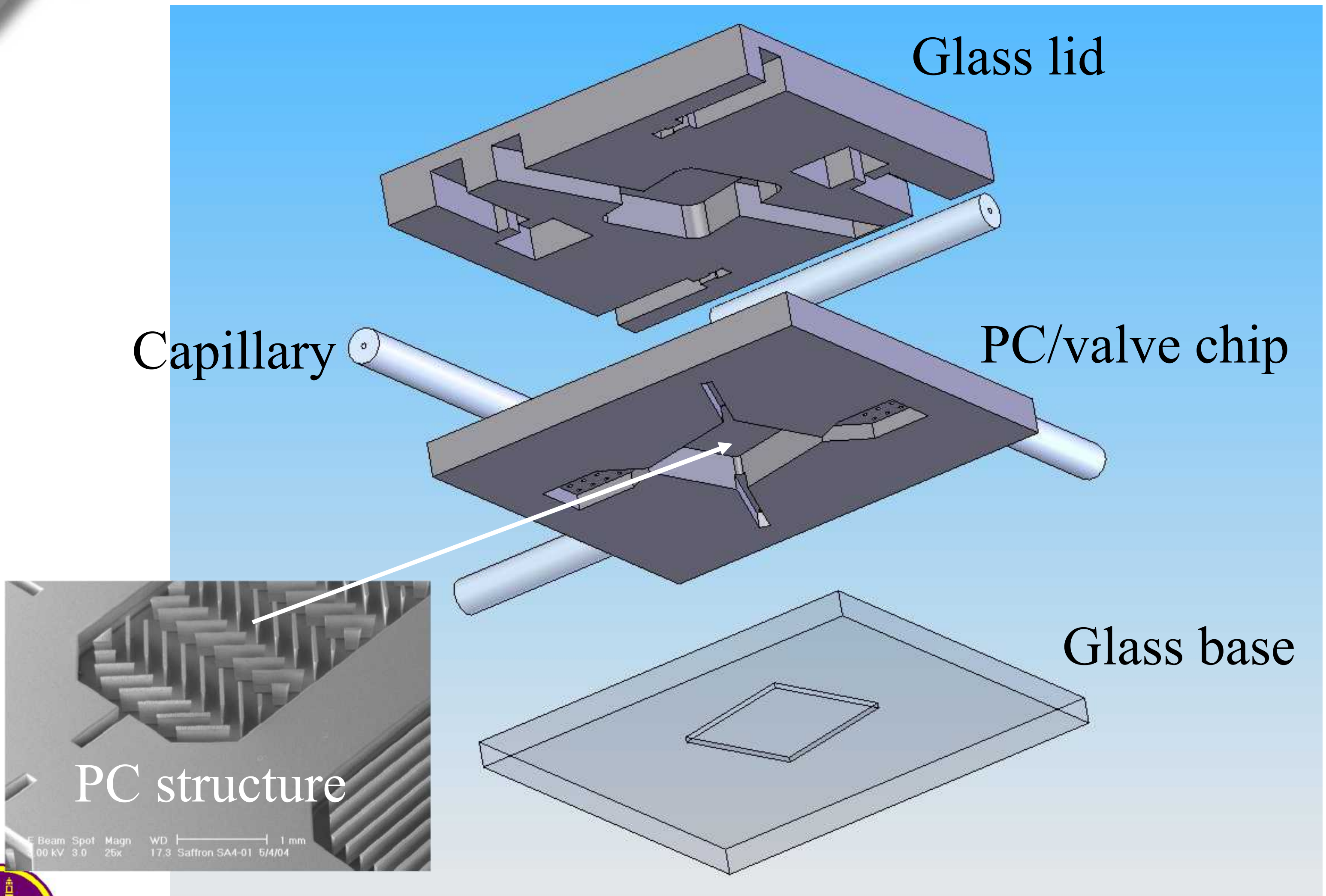
V5 hi / low

Hybrid Integration

MEMS valves on PC chip limit inlet volume



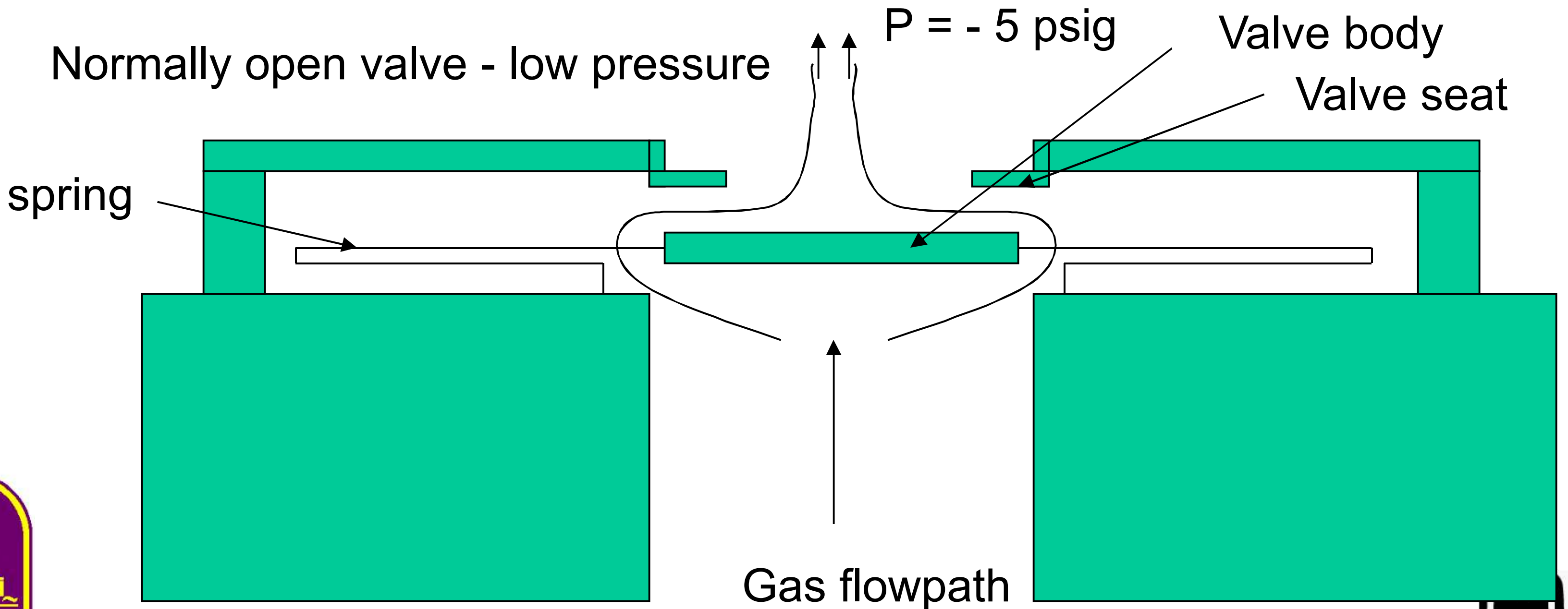
Exploded view from the bottom



Passive Offset Check Valve design concept (normally open valve)

- Open one-way at low pressures
- Closed *in the same flow direction* at higher pressures
- A check valve with an offset.

- Our design uses a soft spring with properly selected stiffness, matched to:
  - Pressure requirement
  - Flow requirement
  - Orifice size

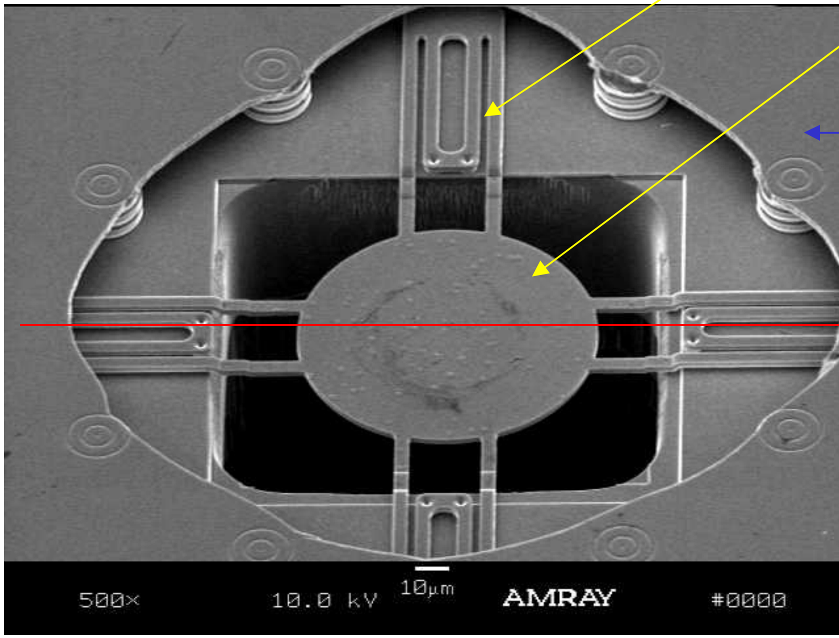


Valve 2 - SUMMiT™ design and fabrication

Valve size ~400 μm²

Spring

Valve body



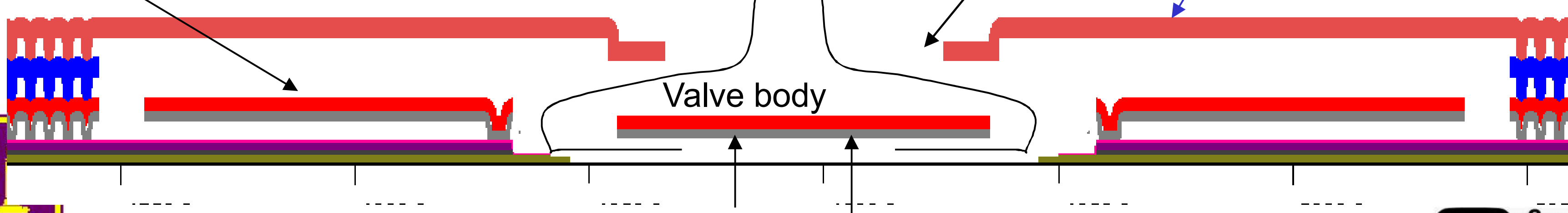
Cross section

Upper poly-Si layer, which defines the valve orifice, is cut away in the micrograph

Valve orifice

Spring attachment

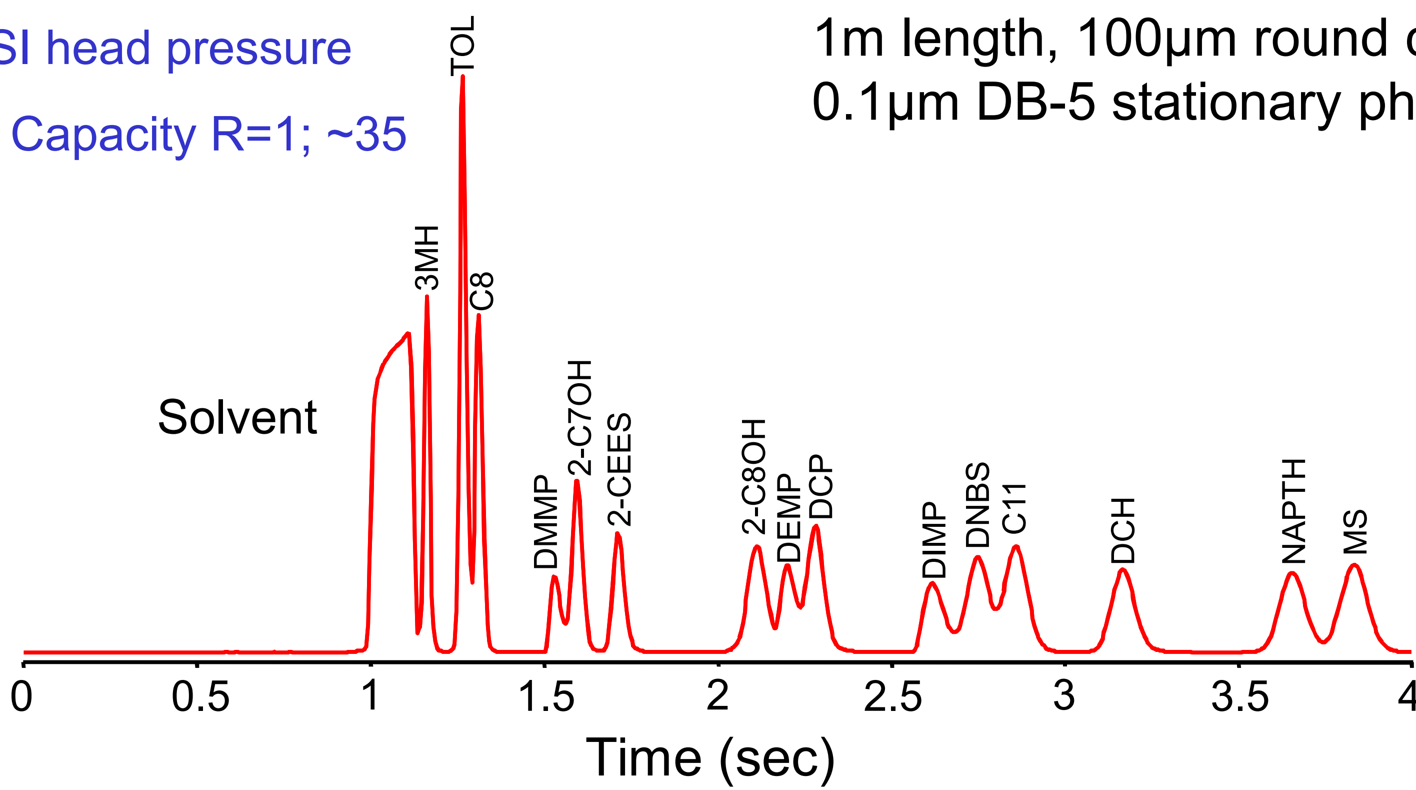
Gas flow



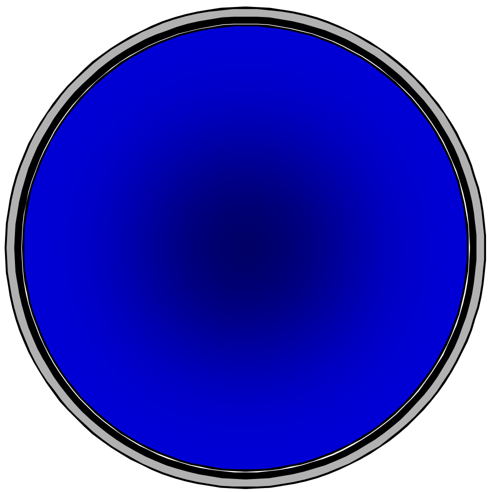
Separation of 16 Compounds in < 4 sec

- Temperature Programmed from 59 to 87 °C
- 30 PSI head pressure
- Peak Capacity R=1; ~35

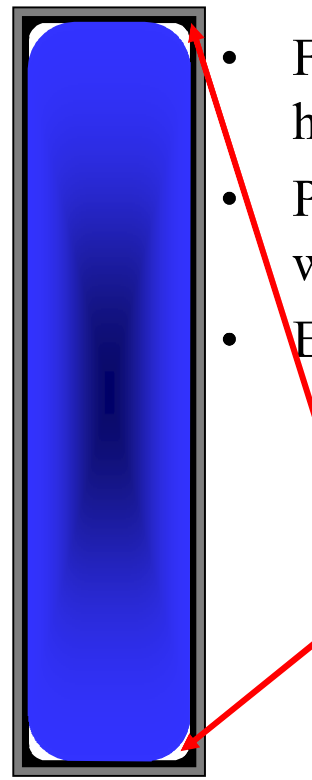
8 CWA simulants
8 interferents
1m length, 100µm round column
0.1µm DB-5 stationary phase



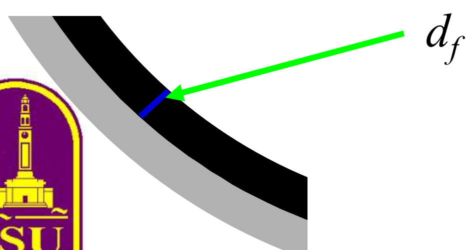
Round vs. HARM columns

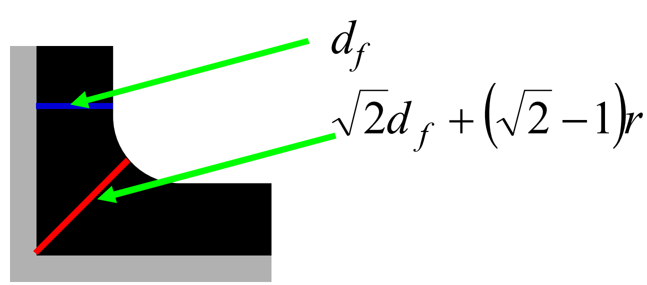


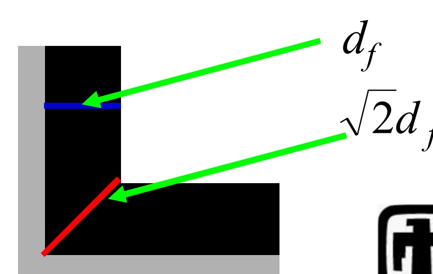
- Flow restriction and performance limited by radius
- Film deposition is uniform

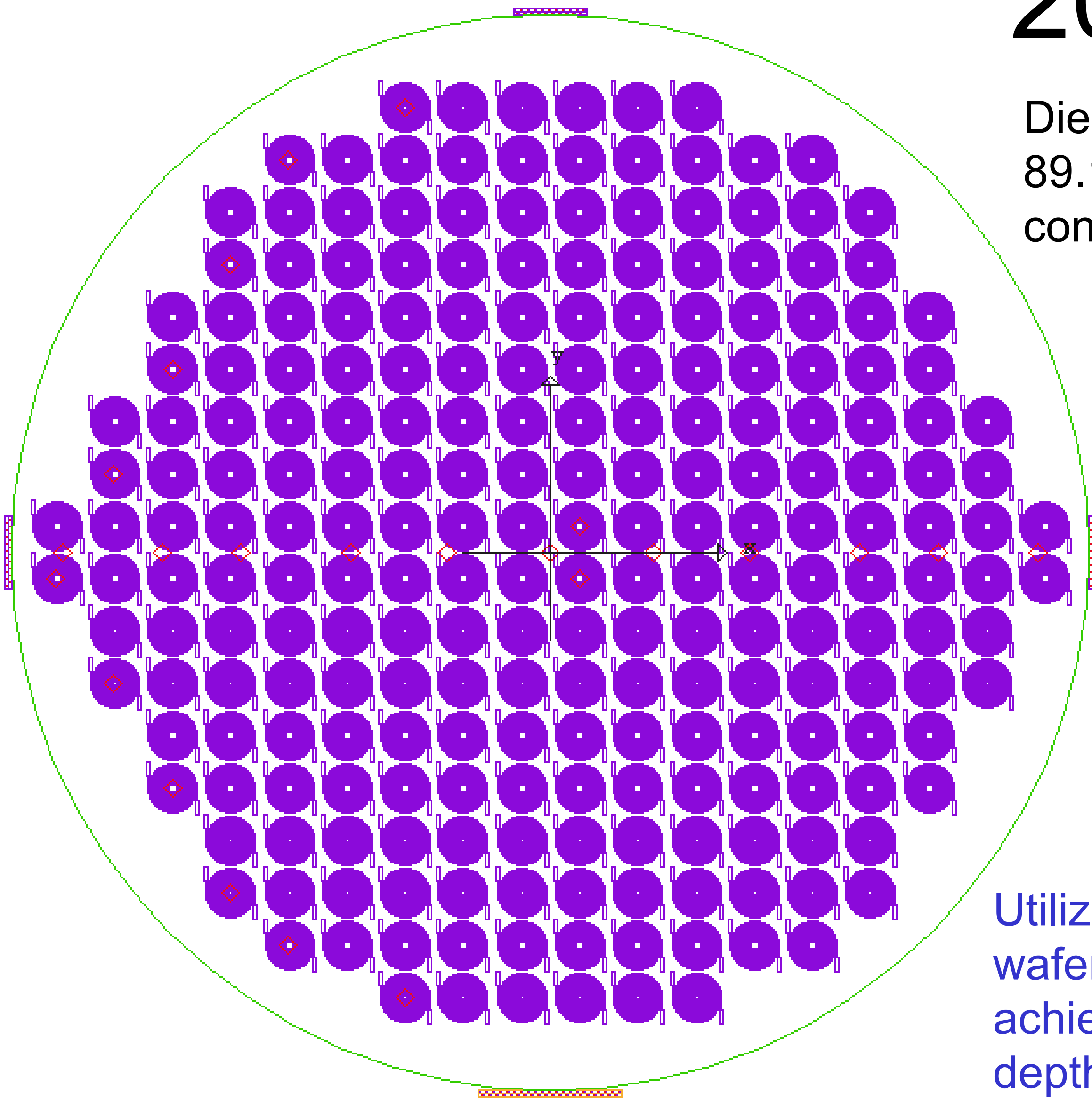


- Flow restriction controlled by height
- Performance limited by width
- End effects
  - Film deposition often results in thicker phases in the corner
  - Dead spaces in corners









2090 GC

Die 1: 20 um wide, 20 um wall, 89.16 cm length between edge connections; 98 occurrences

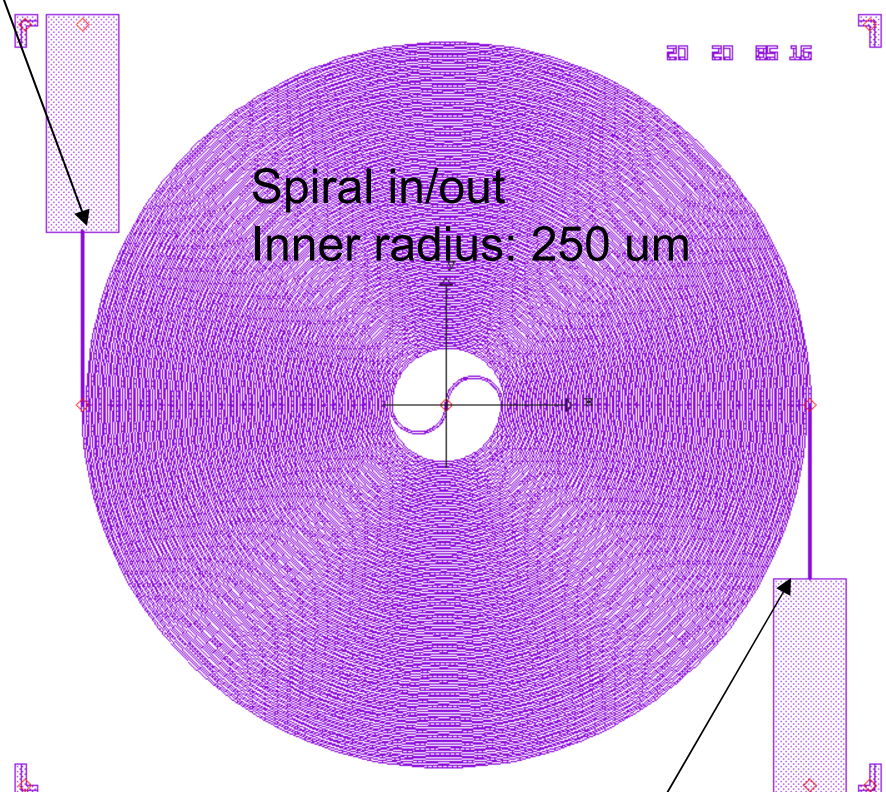
Die 3: 20 um wide, 30 um wall, 73.58 cm length; 68 occurrences

Die 2: Like Die 1 with slight taper before edge connections; 94 occurrences

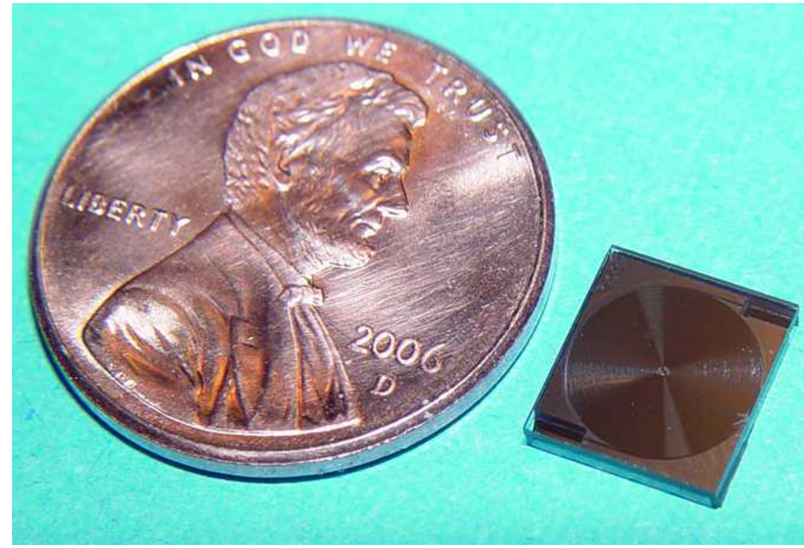
Utilize BOX layer of SOI wafer as etch stop to achieve required column depths

Sample Closeup: Die 1 fabricated on 20 um SOI (1 um BOX, 650 um Si)

Stated lengths are measured between here…



…and here



Die2 has a slight taper

$$Ctot = 0.097\frac{J}{K}$$

Delay layer has arrived and is awaiting processing

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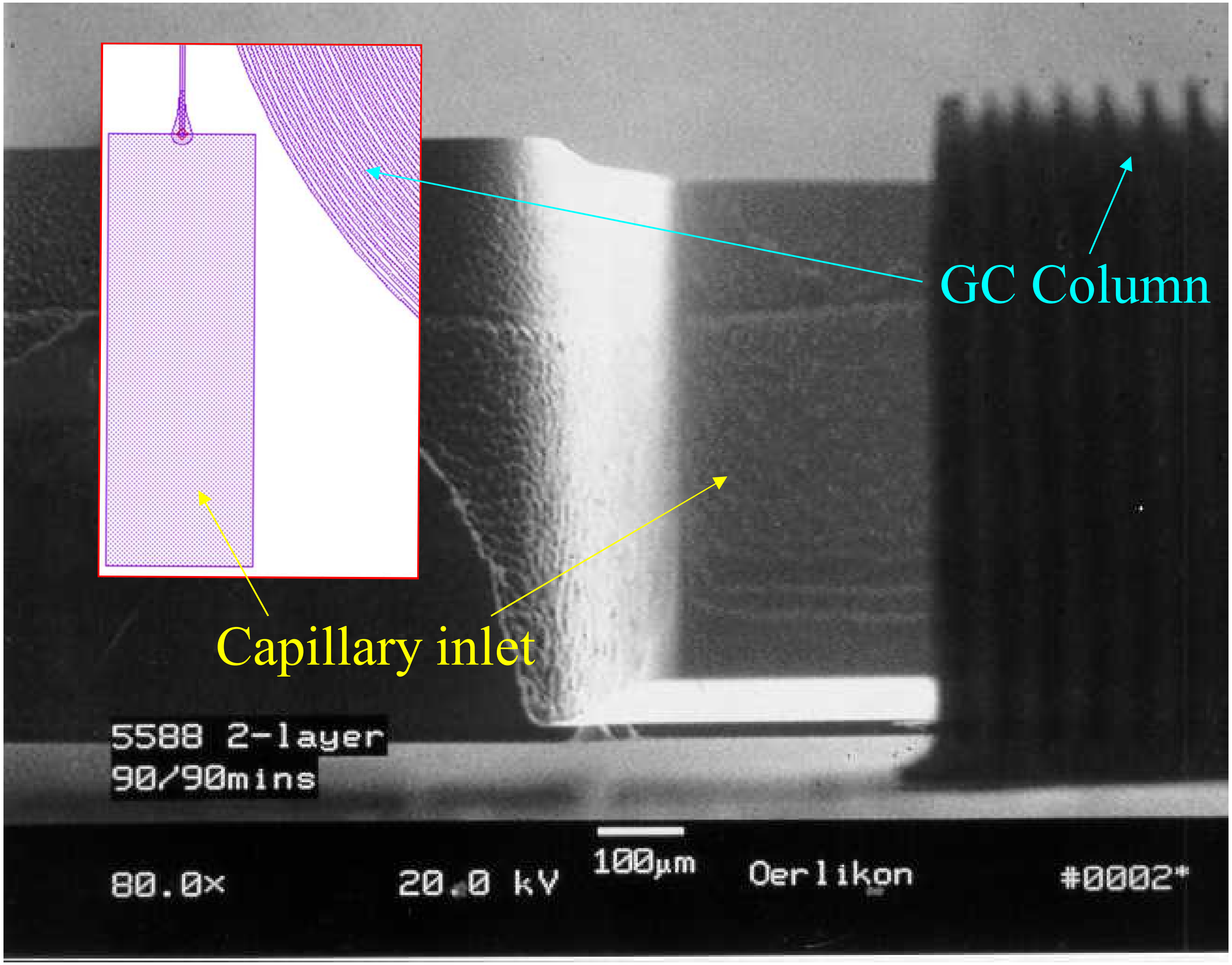
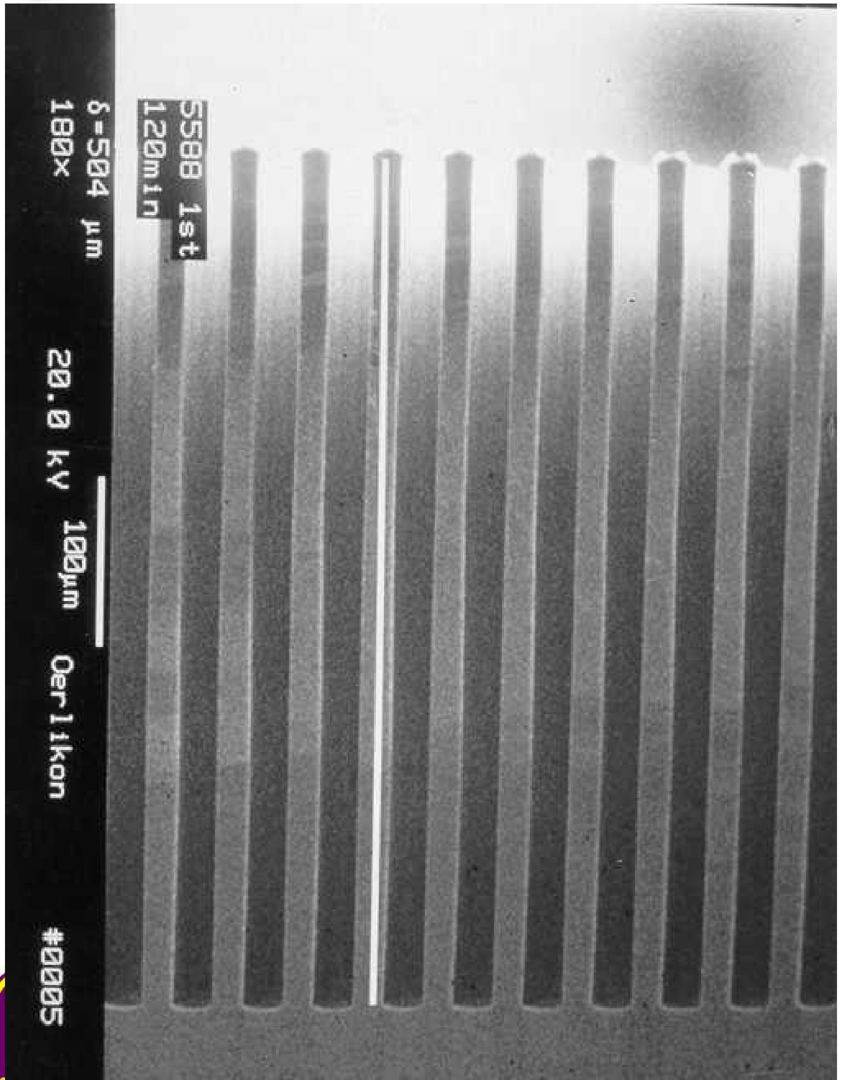
2090 GC test wafer - SEM

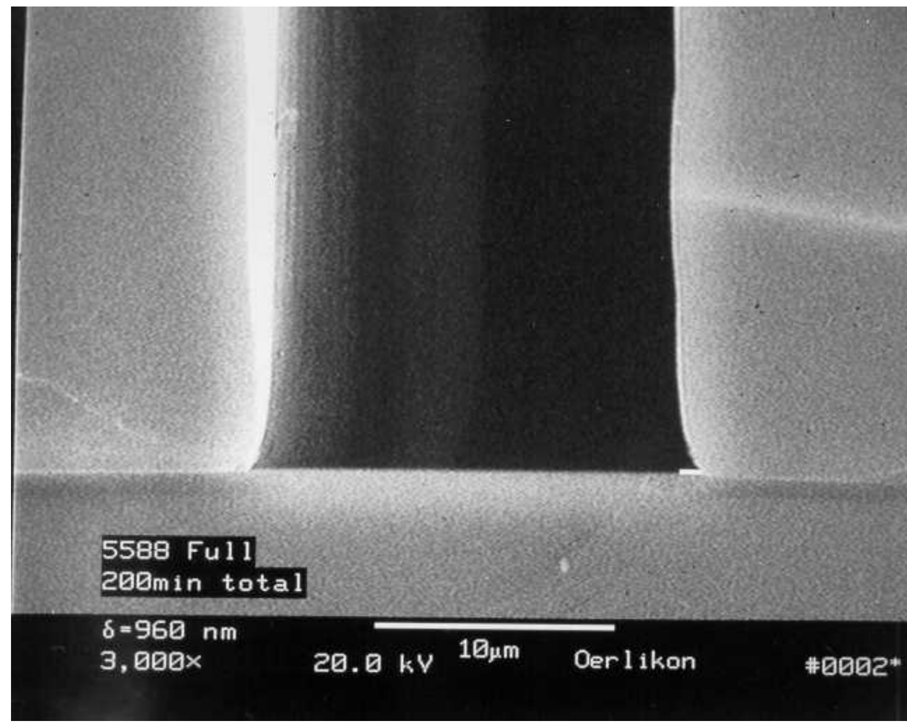


2090 GC test wafer - SEM

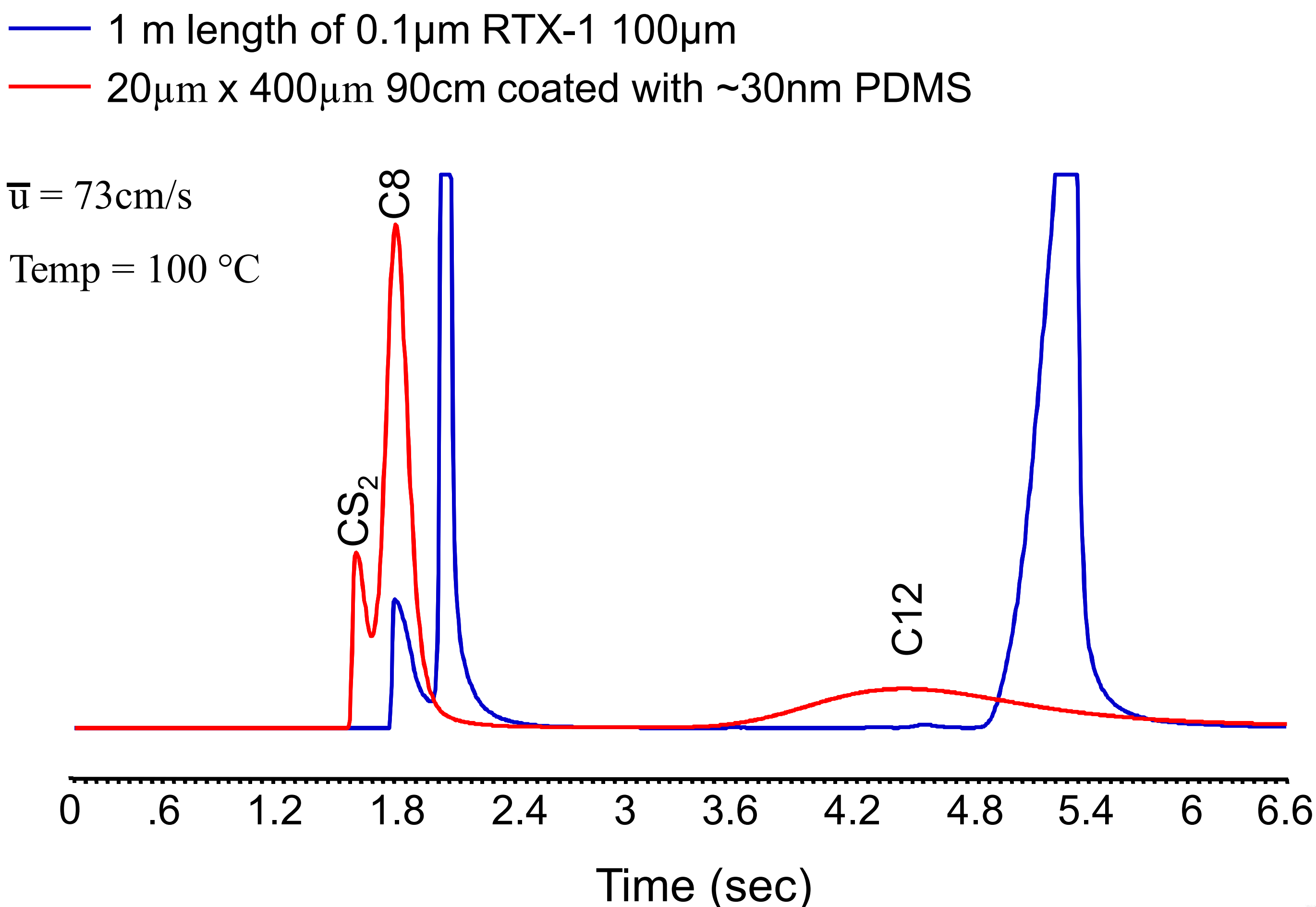
Column walls (first etch)



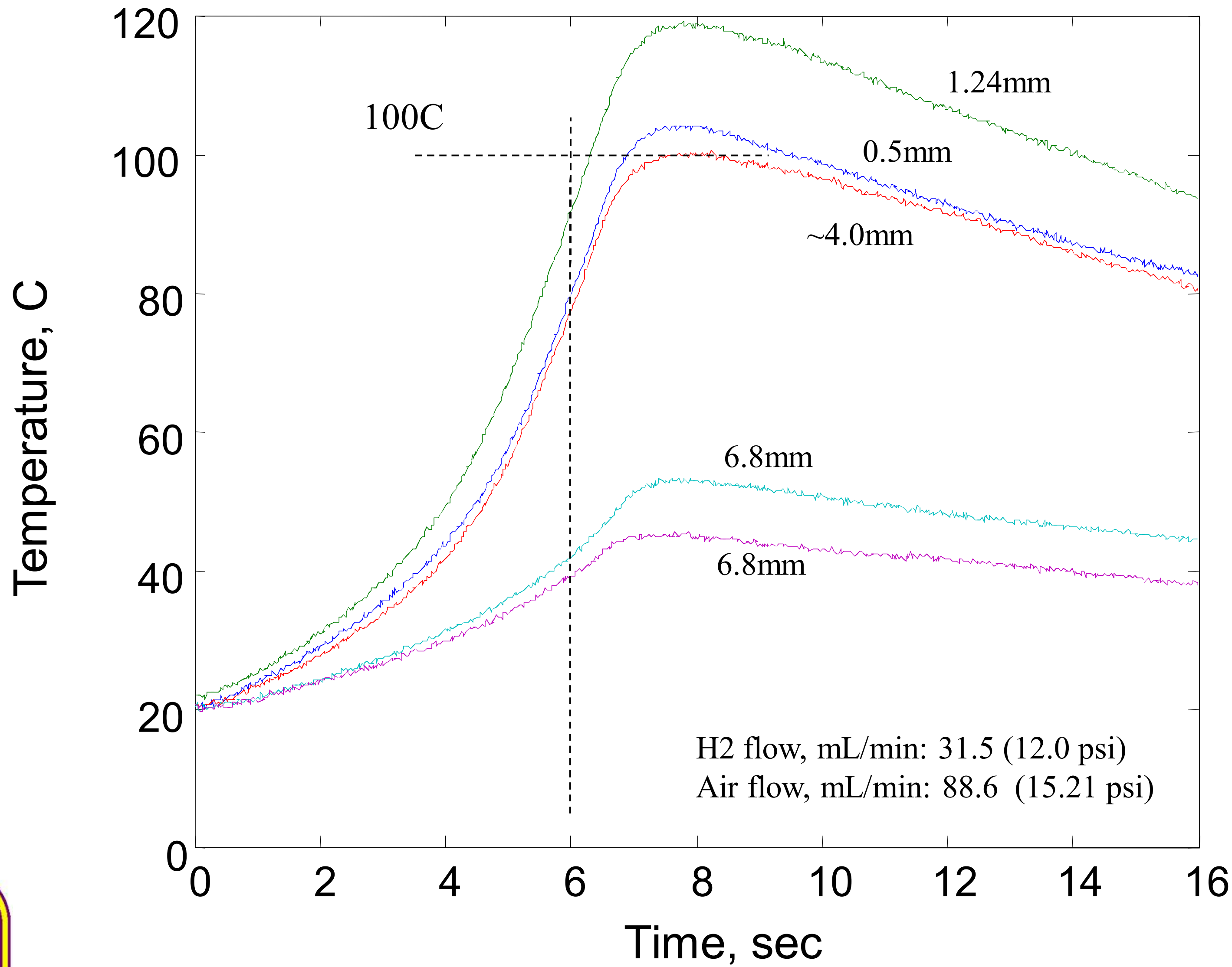
Bottom of column (2nd etch)



Coated Microcolumn Performance

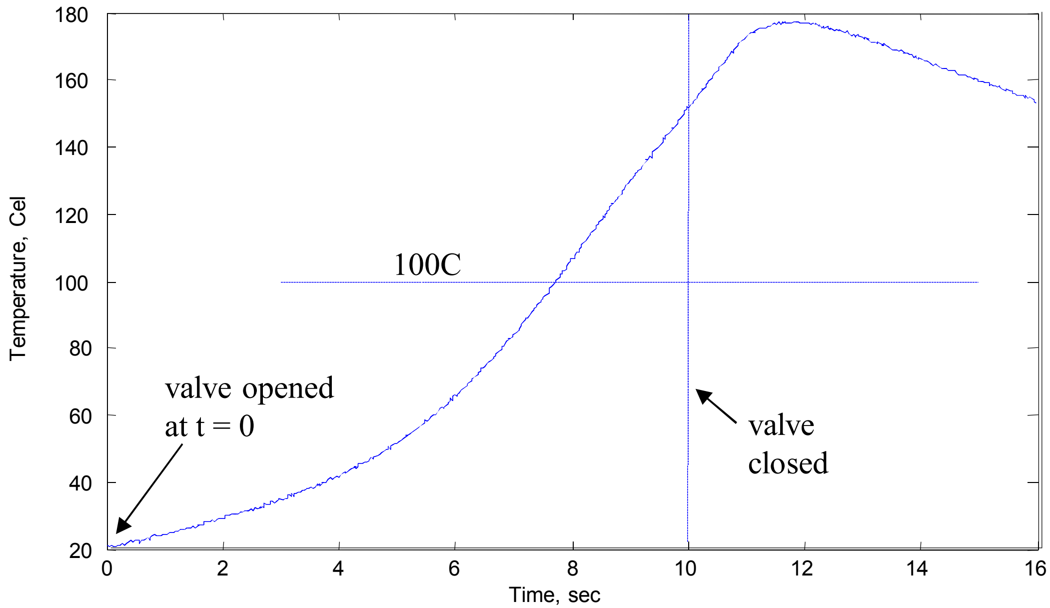


Example data, 2090 GC autocatalytic heating

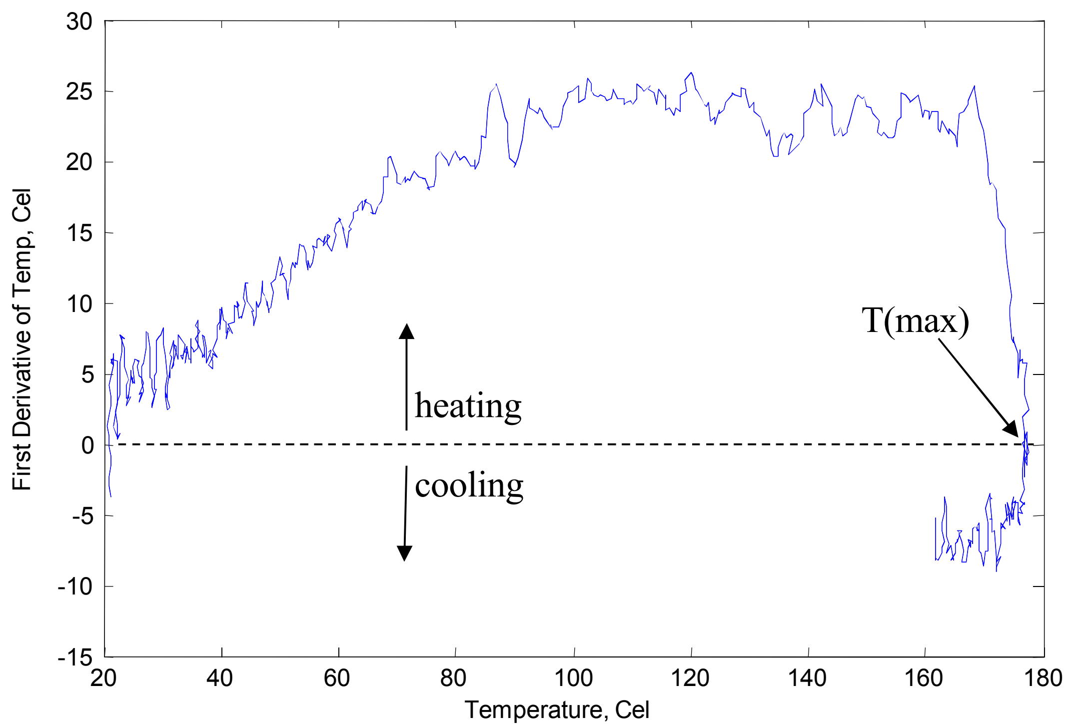


Catalytic GC Heating

- Fuel autoignites
- Thermocouple T lags fuel valve switching
- Efficiency ~25%, can be improved with “burner” design



dT/dt vs. T



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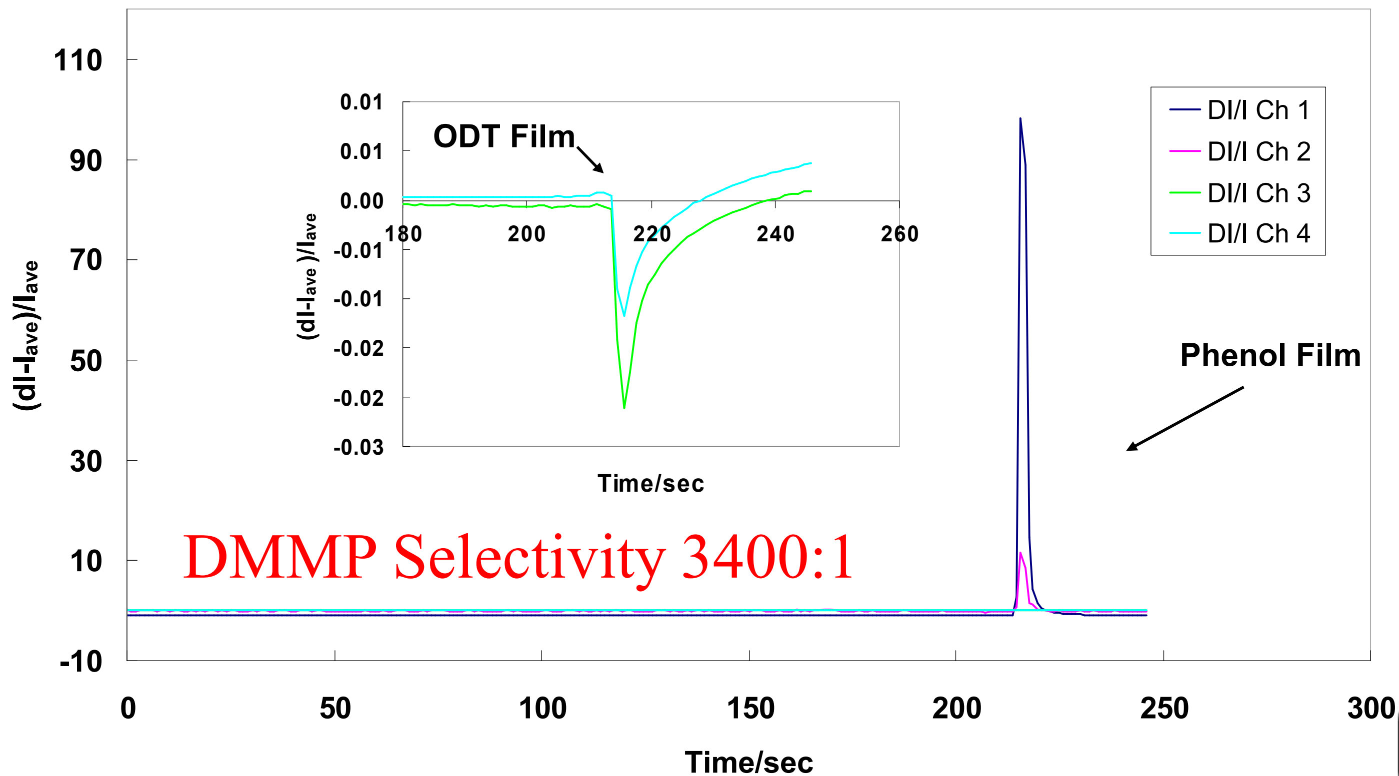
Initial Vapor sensing of DMMP using a protected phenol

Our initial observations during exposure to DMMP show:

- **Protected phenol-Au films have dramatically increased conduction (molecular electronic effect)**
- **Control ODT-Au films have a slight decrease in conduction (swelling)**
- **10^{-4} J per detector channel per analysis!**

DMMP vapor from Tenax PC using Boc Protected Phenol Molecule as Ch 1 and Ch 2 and ODT as Ch 3 and Ch 4 both with Au nanoparticles



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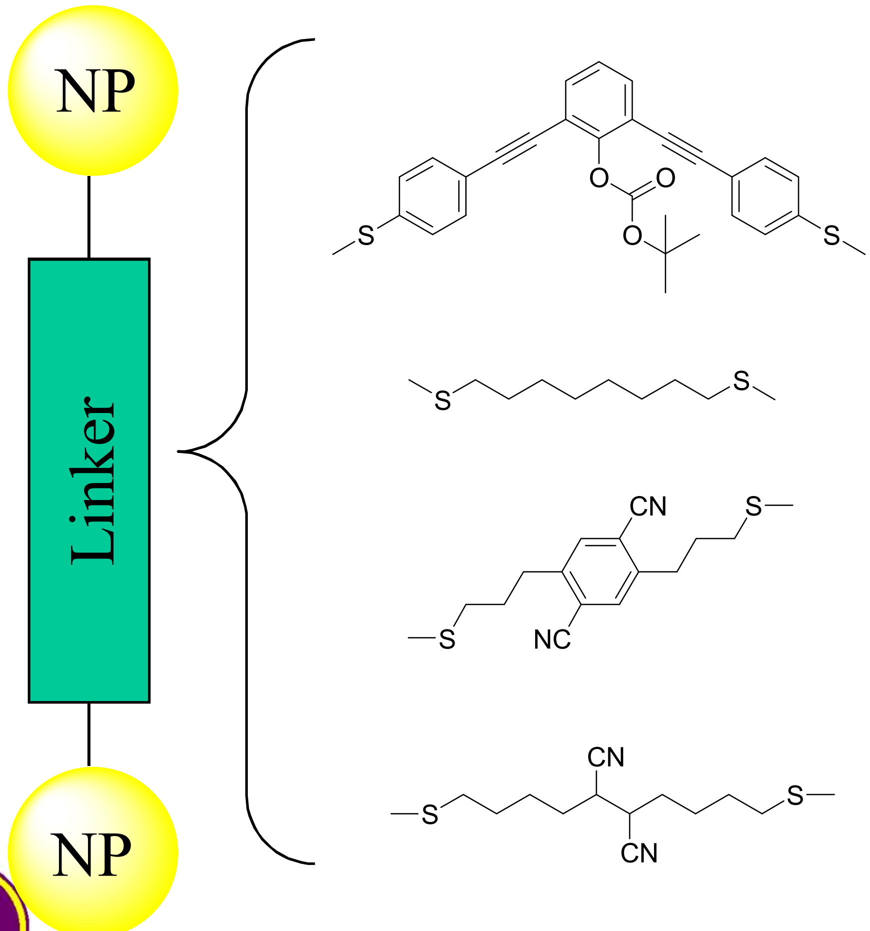
Additional Sensor Channel Candidates

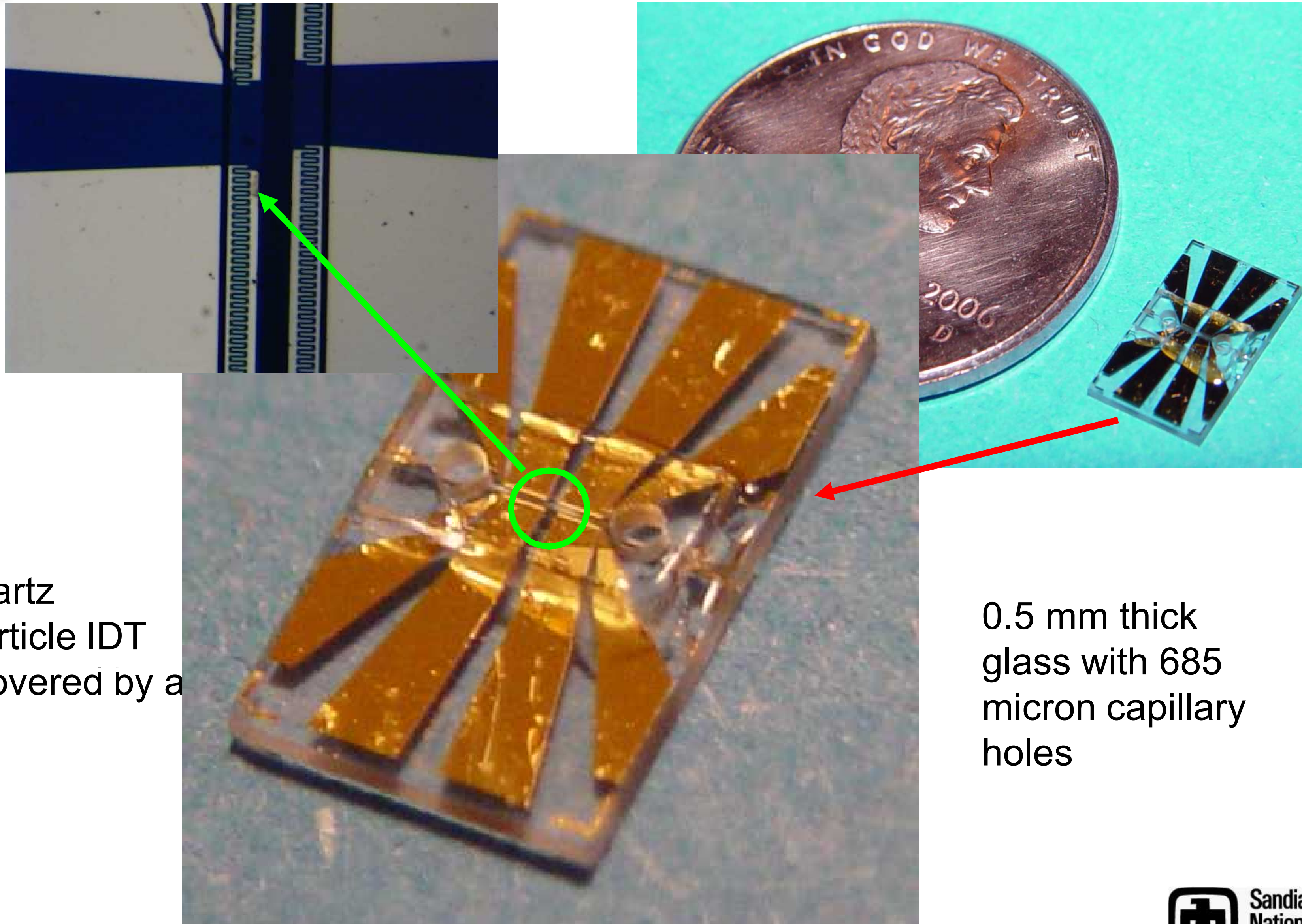


•Phosphonate-selective
•Electron hopping?

Swelling mechanism, nonpolar

•Swelling mechanism
•Vary polarity, polarizability
•Changing partition coefficients adds information to array response, increasing analytical power

Nanoparticle IDT Arrays

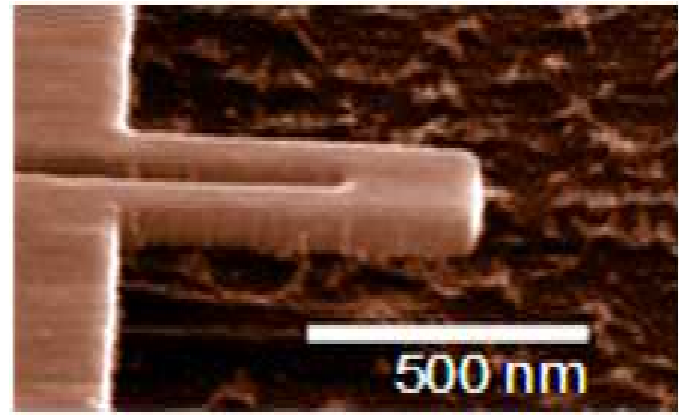


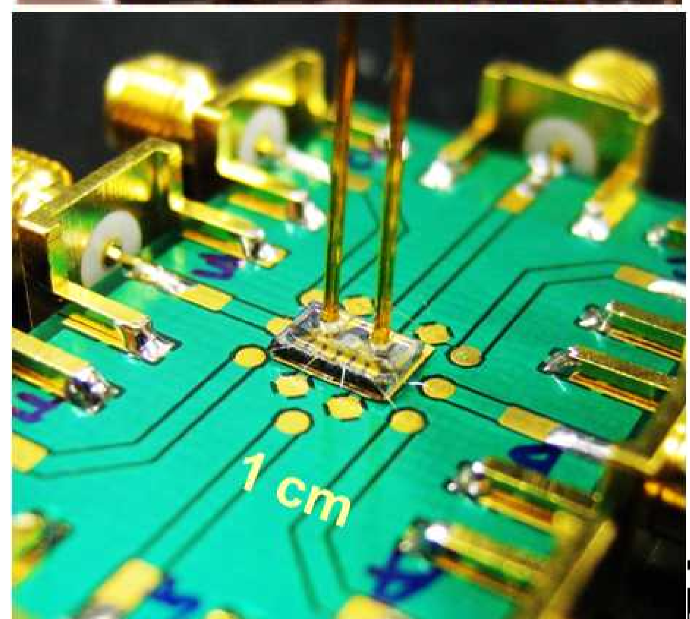
Two quartz nanoparticle IDT chips covered by a flow lid

0.5 mm thick glass with 685 micron capillary holes

CalTech - NEMS Cantilever Resonators for GC Detection

- **100 zg** Noise floor at ambient temperature and pressure
- Low Power < 1μW
- High Frequency > 1GHz
- High Q values even in ambient air because of low active mass





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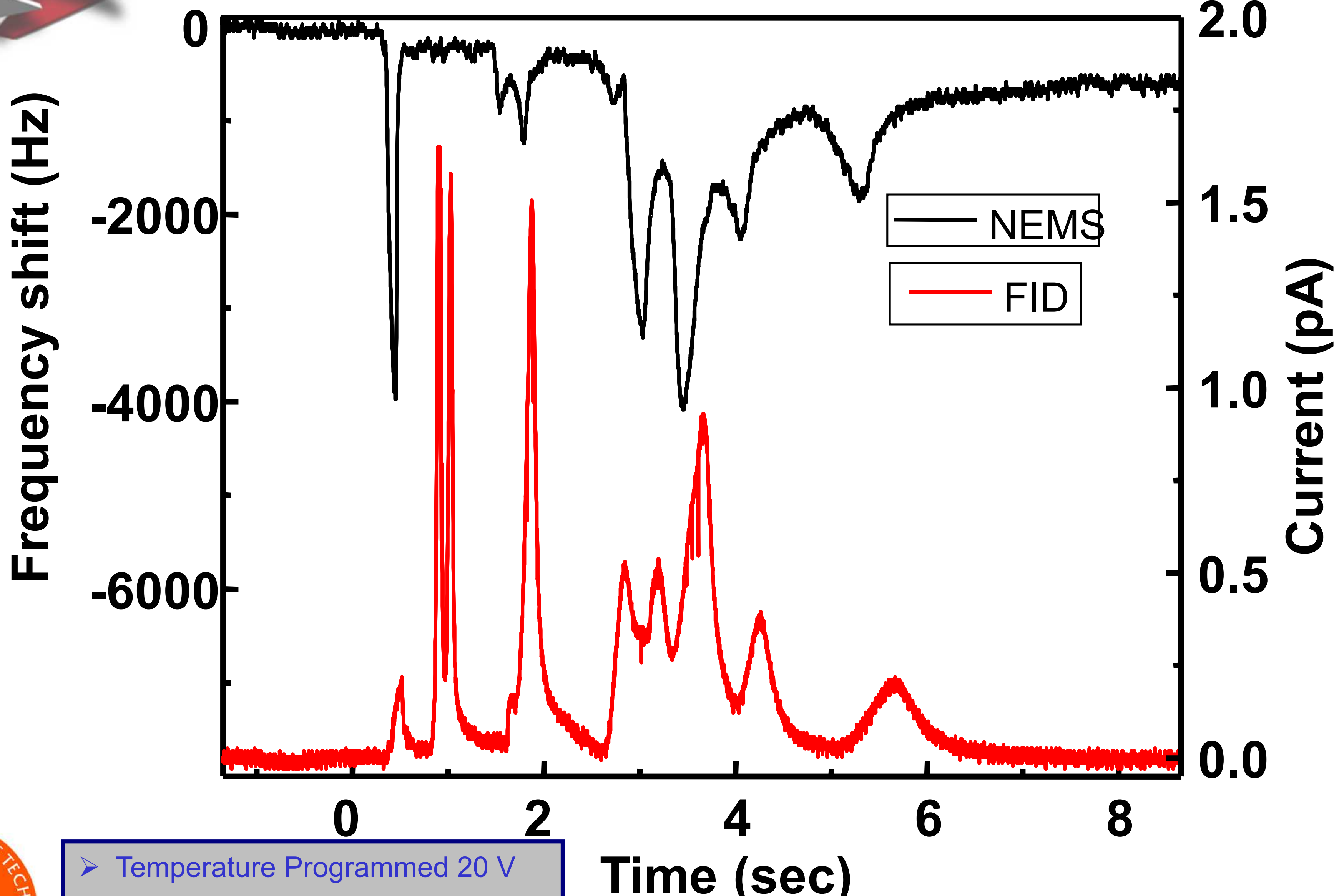
Fast GC with NEMS: 14 peaks in 6 seconds



- Temperature Programmed 20 V
- 30 PSI head pressure
- 8 simulants, 6 interferents

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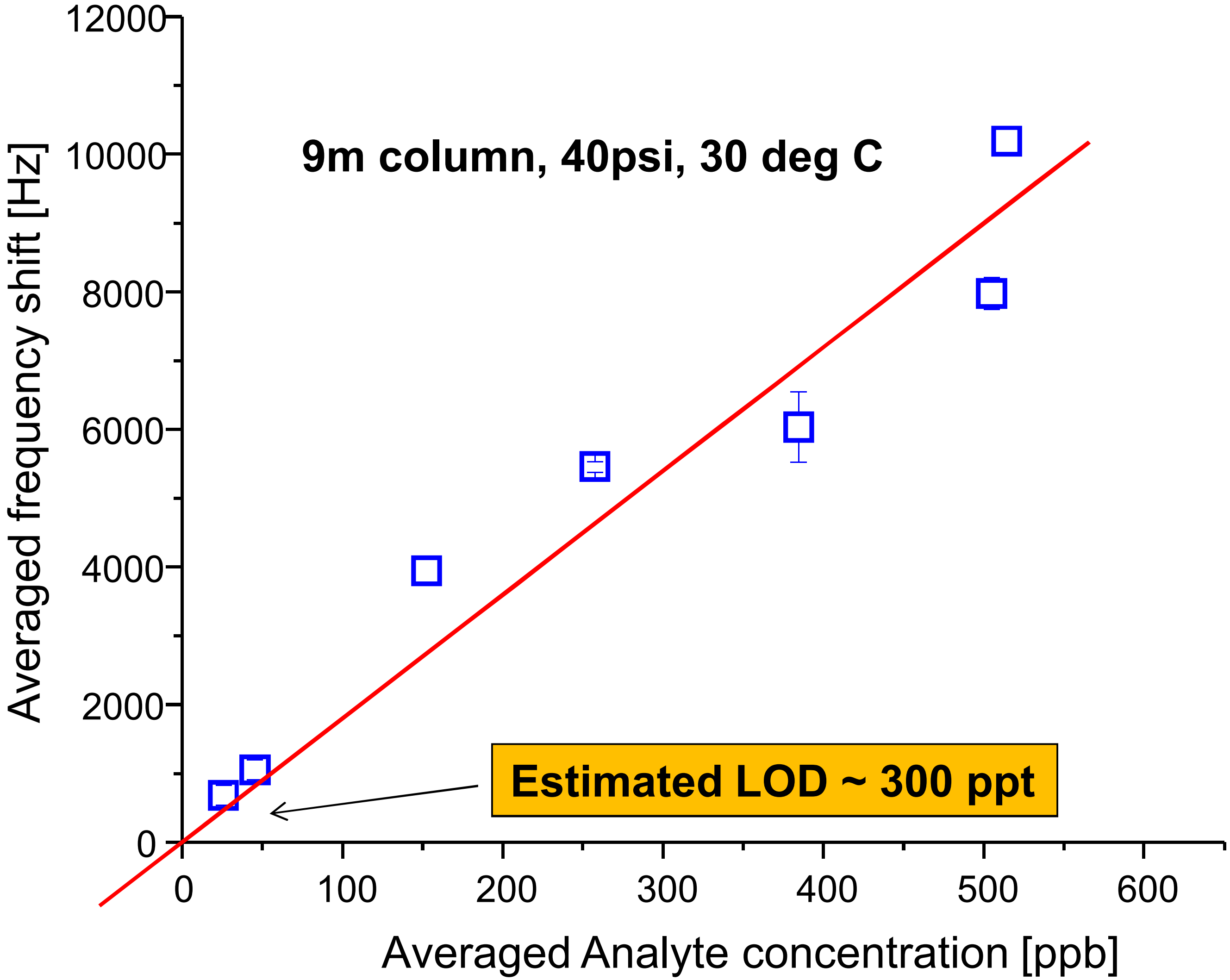
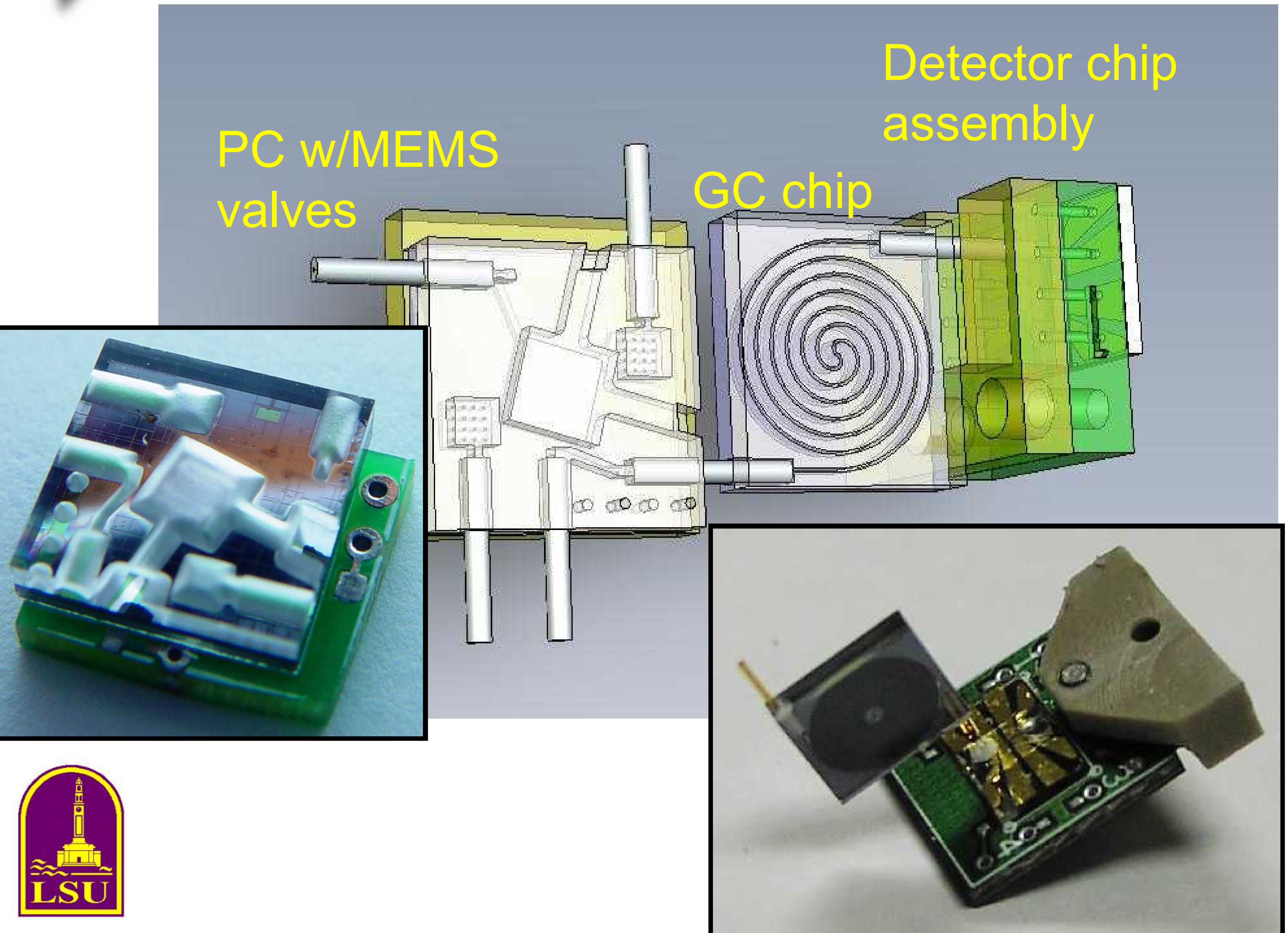
Detector Response

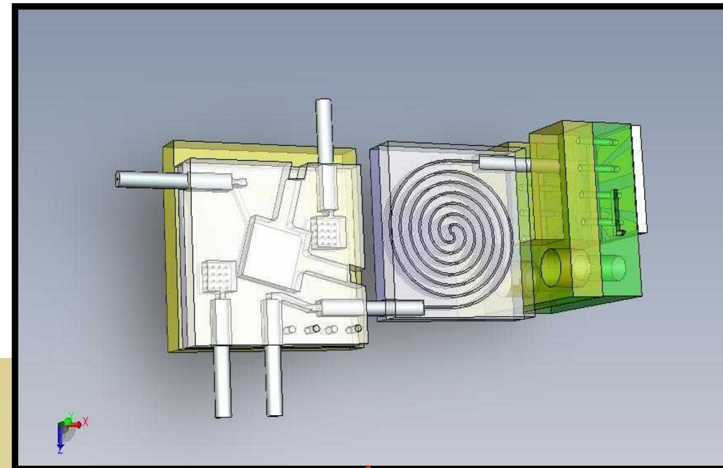


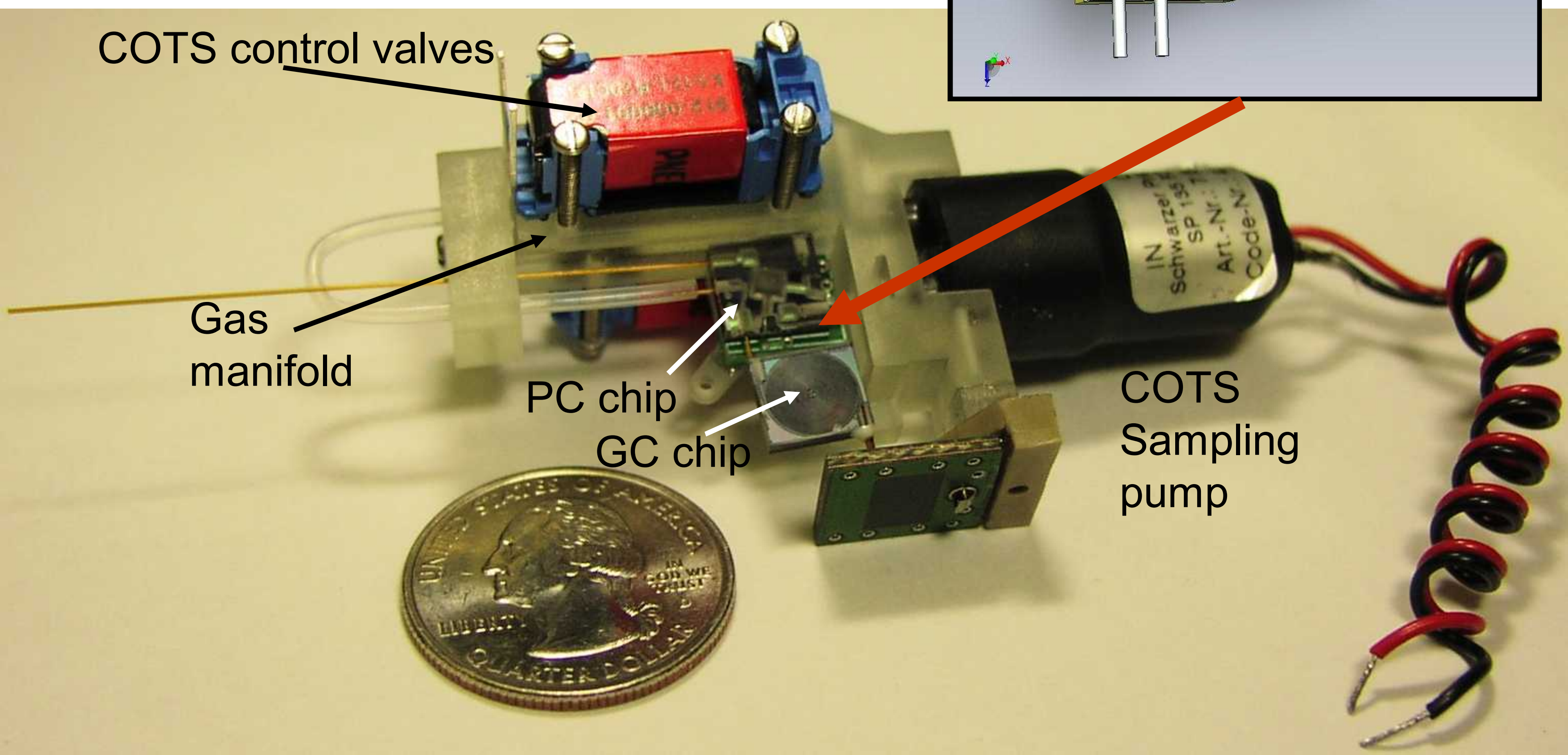
MicroFluidic Sub-Assembly



Total Fluidic System Assembly

Micro Fluidic Assembly





Future Work

- Modify fabrication of column structures to increase yield and minimize “grass” at the bottom of the high aspect channel structures
- Coat and test integrated PC and valve structure
- System testing