



Advanced Technologies for Chemical Weapons Detection and Analysis

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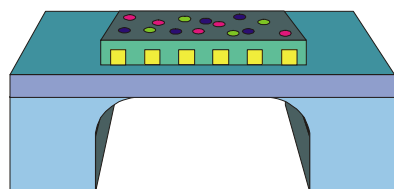
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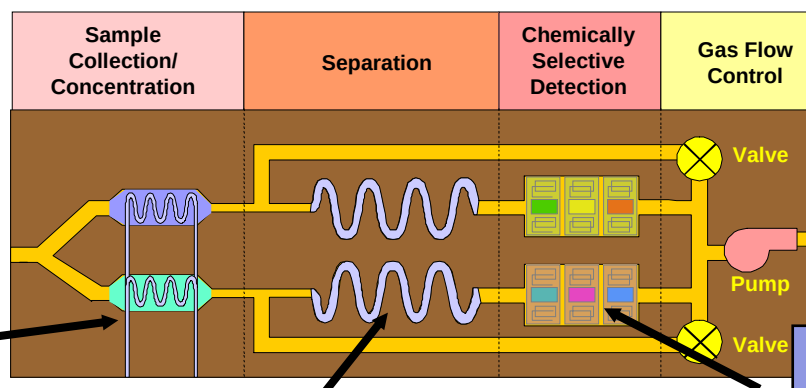
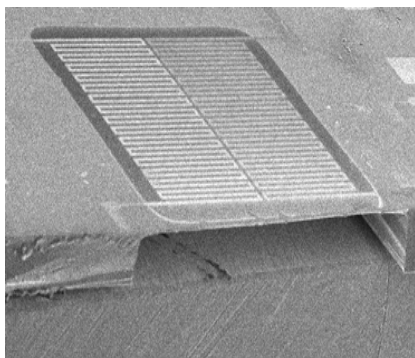
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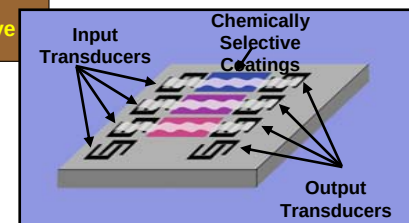
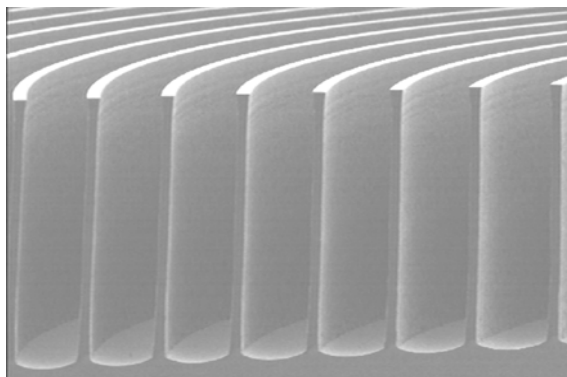
μ ChemLabTM



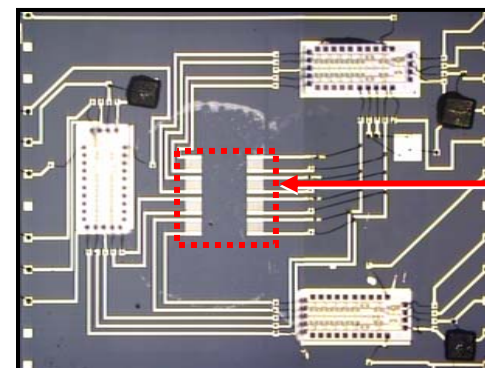
Preconcentrator accumulates species of interest



Gas Chromatograph separates species in time



Acoustic Sensors provide sensitive detection

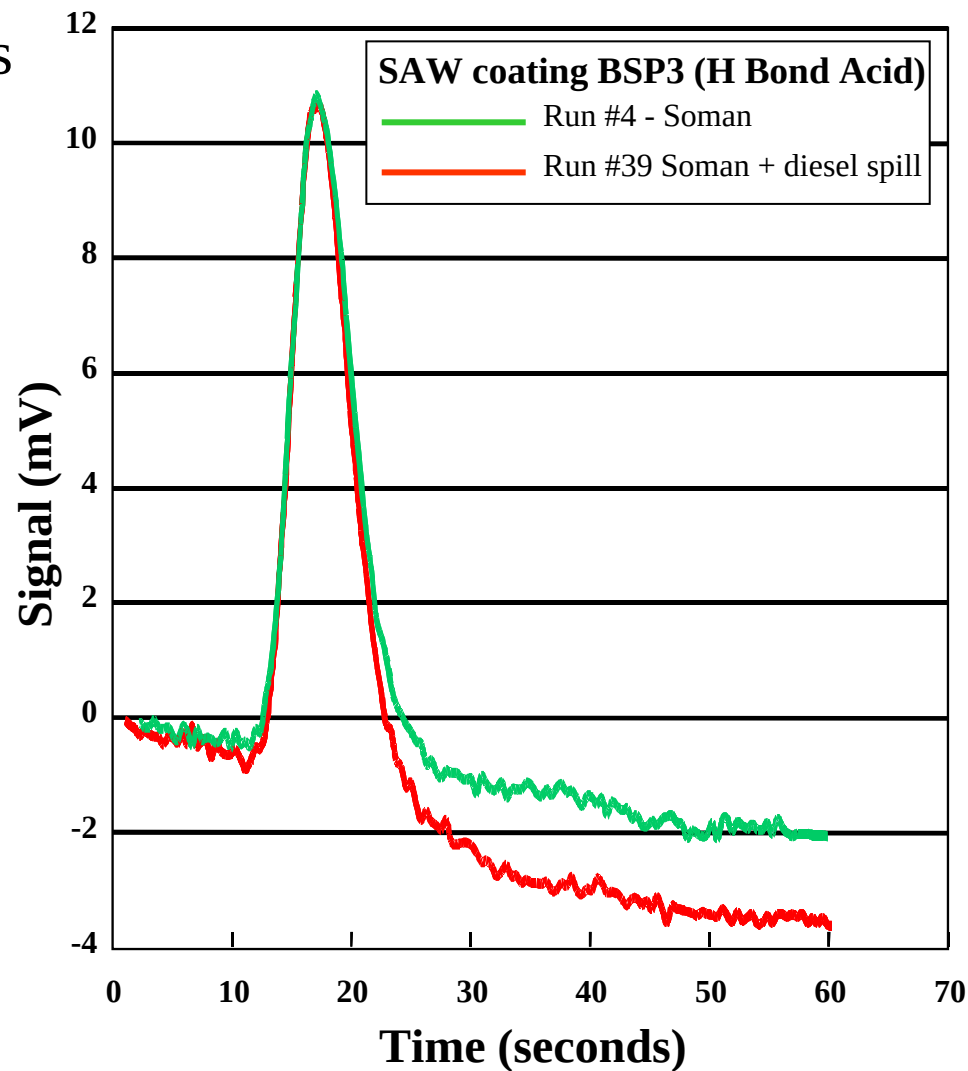
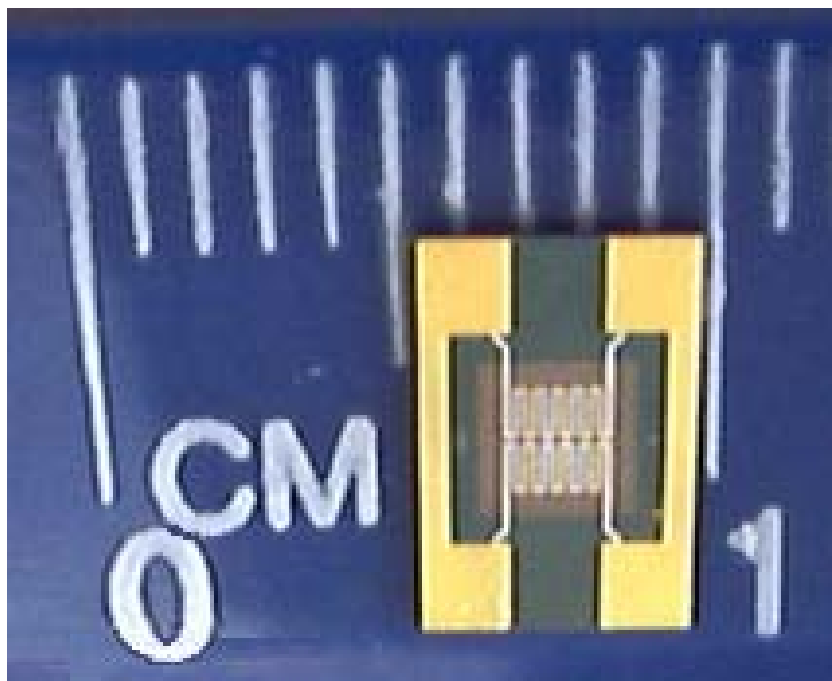


SAW Array



Preconcentrator Selectivity

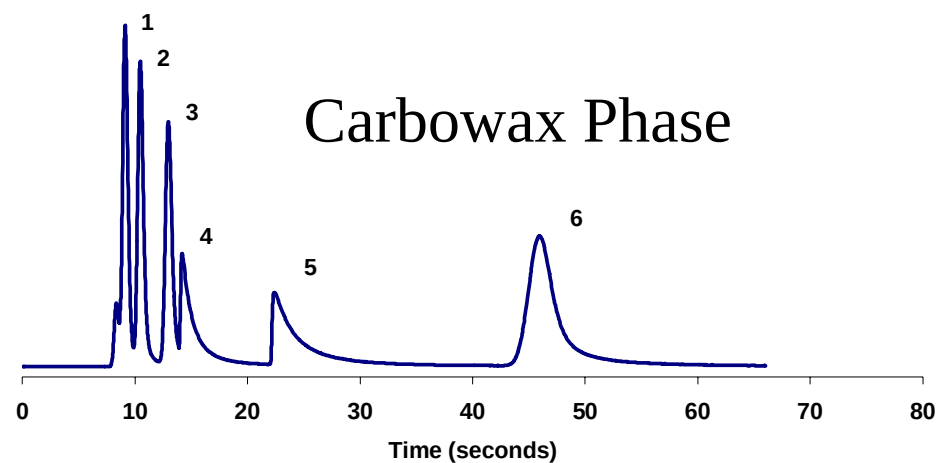
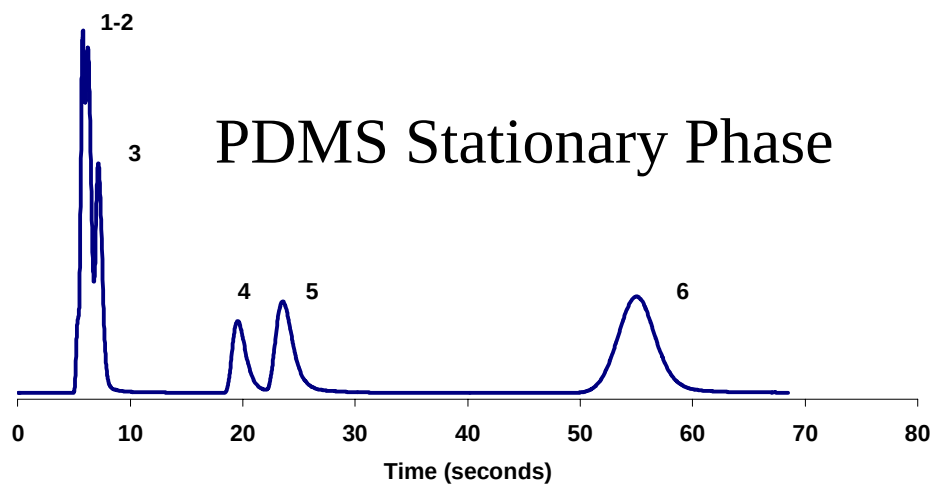
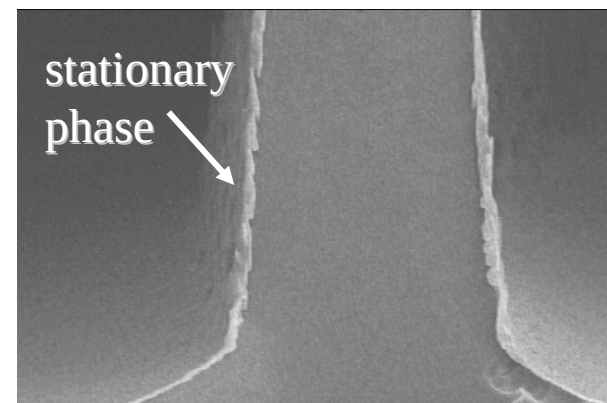
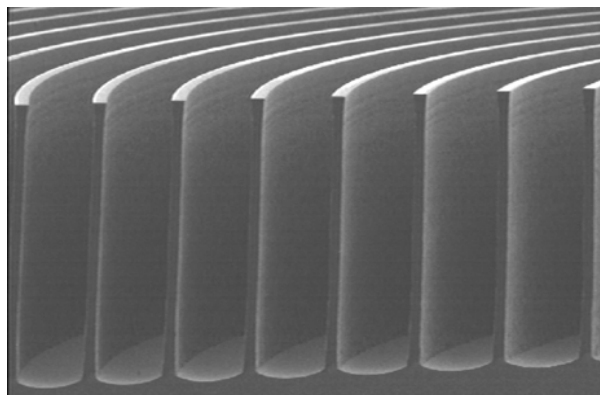
- Adsorbent preconcentrates analytes
- Micro-hotplate rapidly heats to desorb trapped analytes
- Phosphonates selective sol-gel material for CW agents





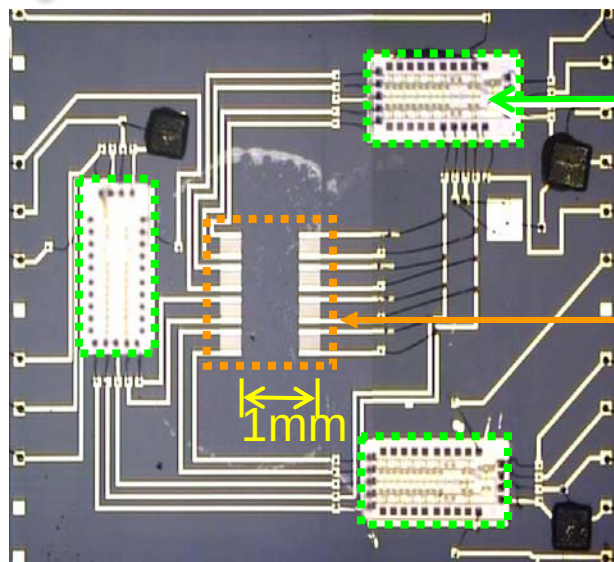
Micro-GC Performance

SEM of Deep Etch Spiral GC Column



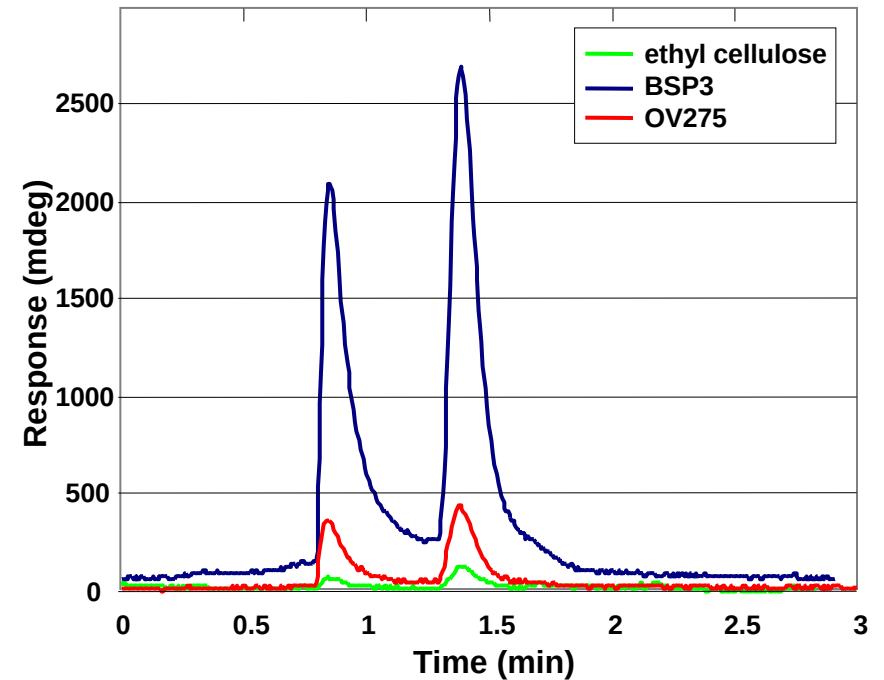
- | | | |
|------------|------------|----------------------|
| 1) benzene | 2) toluene | 3) xylene |
| 4) DMMP | 5) DEMP | 6) methyl salicylate |

SAW Description



GaAs High
Frequency
Circuits

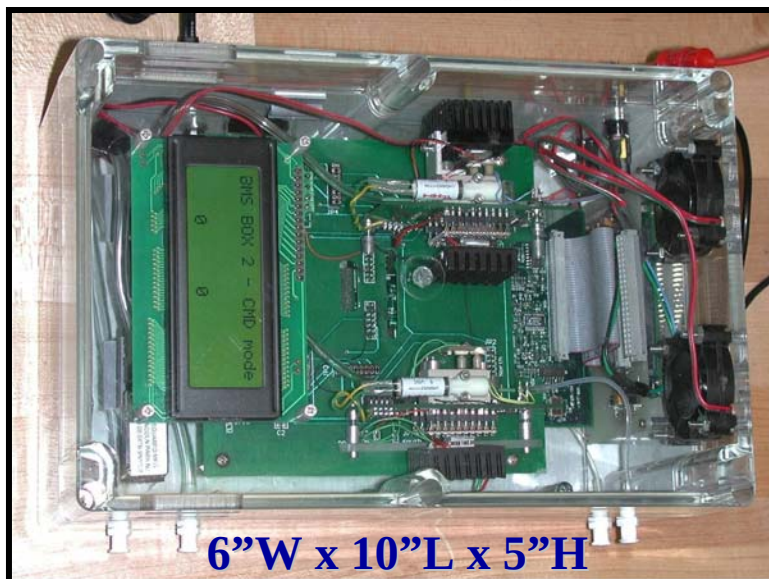
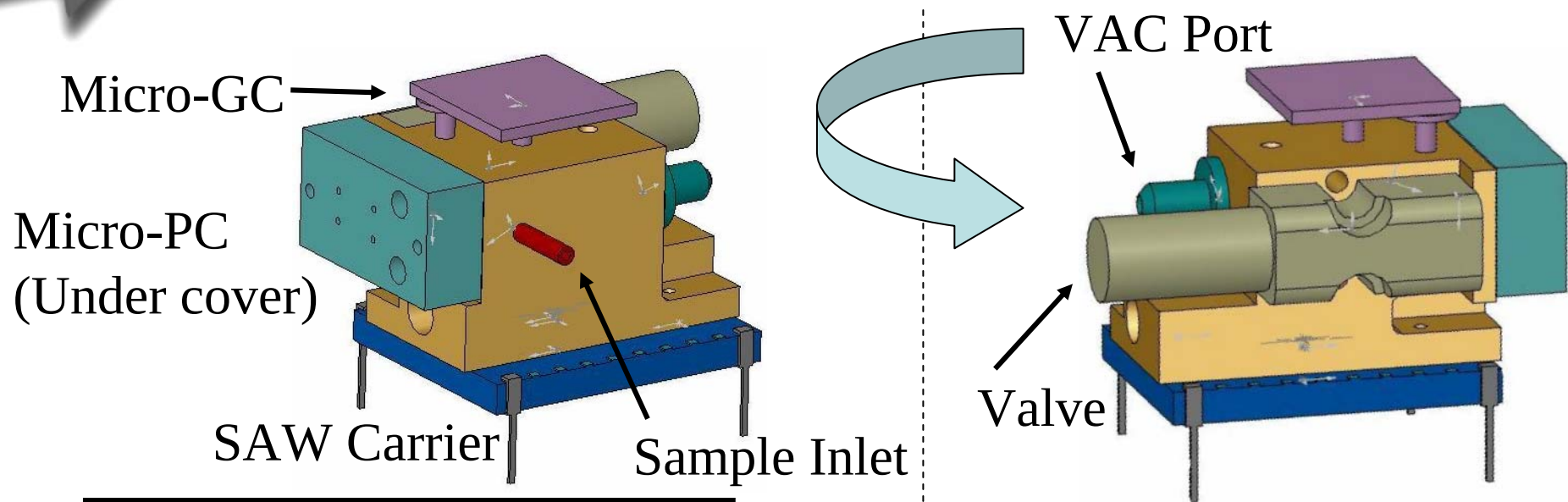
SAW
Delay
Lines



SAW Sensor Array

- Drive electronics lock in on REFERENCE resonance to drive delay lines in array
- Receiver electronics compare phase of drive and received wave frequencies
- Coatings on the delay lines selectively absorb analytes in gas stream over array
- Mass change on the quartz surface affects the phase difference
- Input power 3 VDC at 100 mA
- Output differential -0.9 VDC to $+0.9$ VDC proportional to phase

μ ChemLab Bug

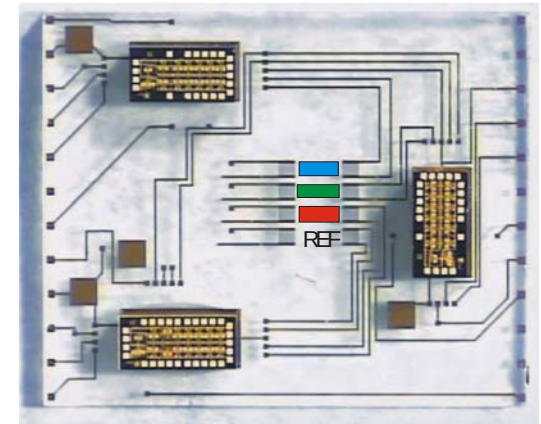




SAW Shortcomings

SAWs Are Great micro-Balances; Only a Few Drawbacks

- Hybrid architecture – Quartz substrate, GaAs electronics
 - Monolithic integration with PC and GC is difficult
 - High labor cost
- 100-500 MHz operating frequency
 - COTS electronics more complicated to use
 - Power hungry (~300 mW for detector)
- Polymer coating is difficult
 - Small application area (0.3 mm x 0.8 mm)
 - Coating must have intimate contact with quartz (little beading, no dewetting)
 - Sensitive to overload
- Finite time for sample absorb/desorb
 - Wider peaks hamper chromatography



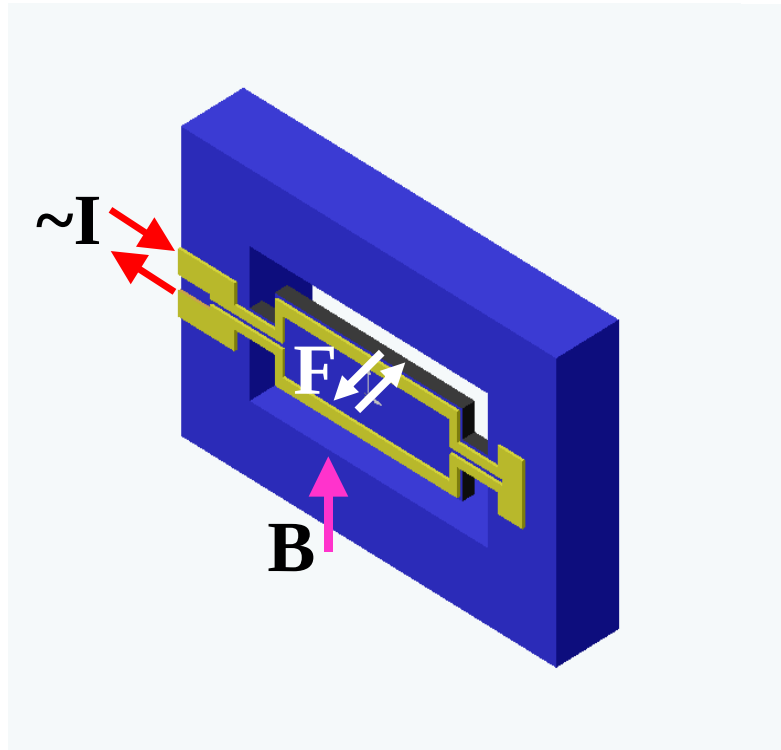


New Micro-Sensors

- Pivot Plate Resonator (PPR)
- Nano-Particle Ligand Bridge Sensor (NPLB)
- Nitrogen Phosphorus Detector (NPD)
 - Thermal Conductivity Detector (TCD)
 - Flame Ionization Detector (FID)
 - Chemiresistors
 - Pellistor Array
- Micro-Calibration Chip



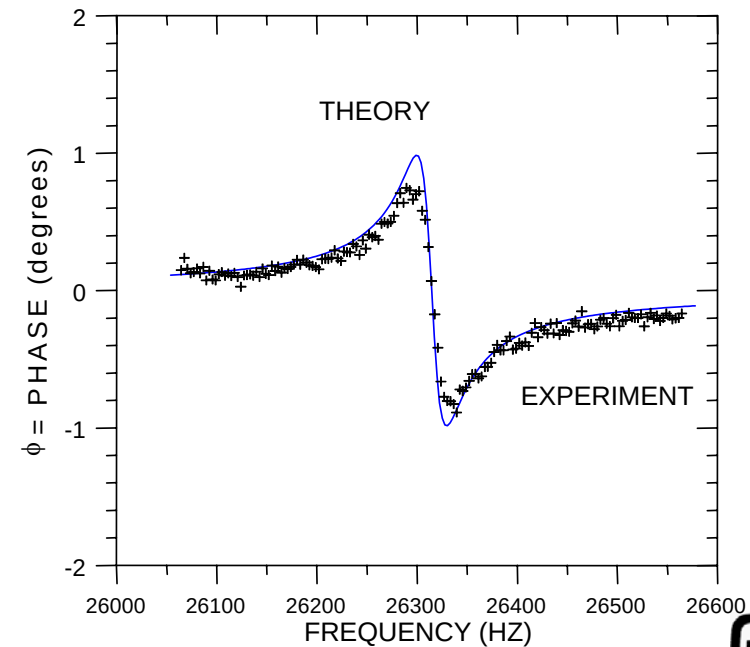
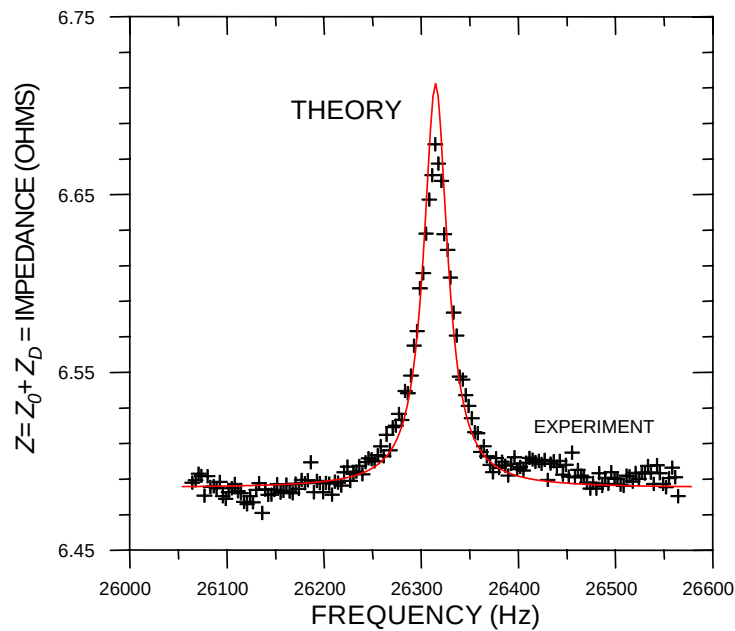
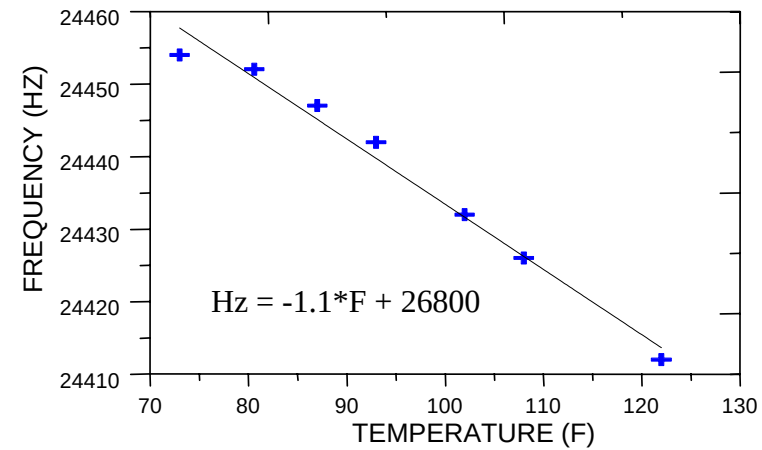
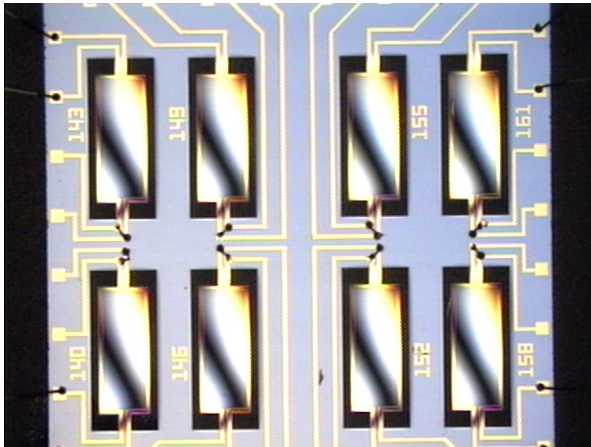
Pivot Plate Resonator (PPR)



- Paddle supported on two pivots
- Pivots provide torsional spring force
- Current in magnetic field imposes a moment on the paddle
- Alternating current drives paddle into resonance
- Motion of paddle creates back-EMF
- Mass changes on paddle alter the resonant frequency
- Damping changes on paddle alter the amplitude of oscillation



PPR Testing

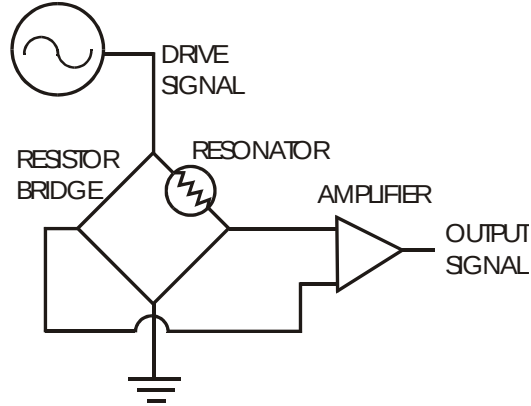


PPR – Pivot Plate Resonator



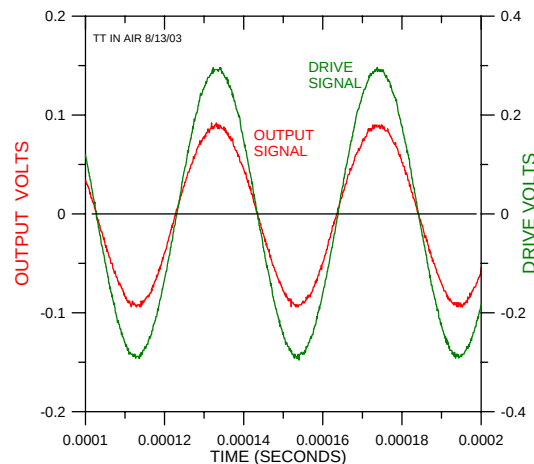
Mass Loading of a PPR

VARIABLE FREQUENCY
WAVEFORM GENERATOR

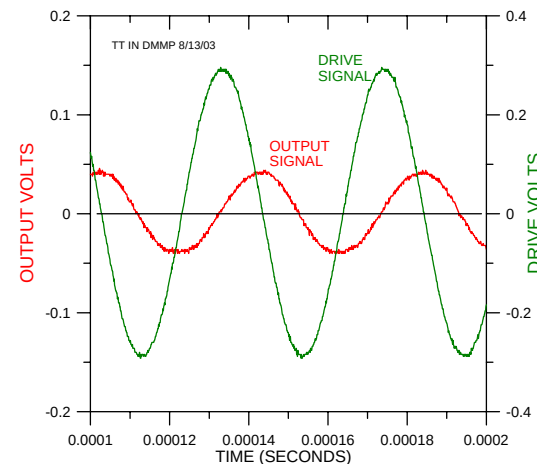


- Monitor phase for low level detection
- 10 ng causes about 90 degree phase shift
- Sensitivity about 9 degrees/ng
- Compare to minimum SAW sensitivity of about 0.1 ng

Coated paddle with no analyte



Response to Vapor Exposure



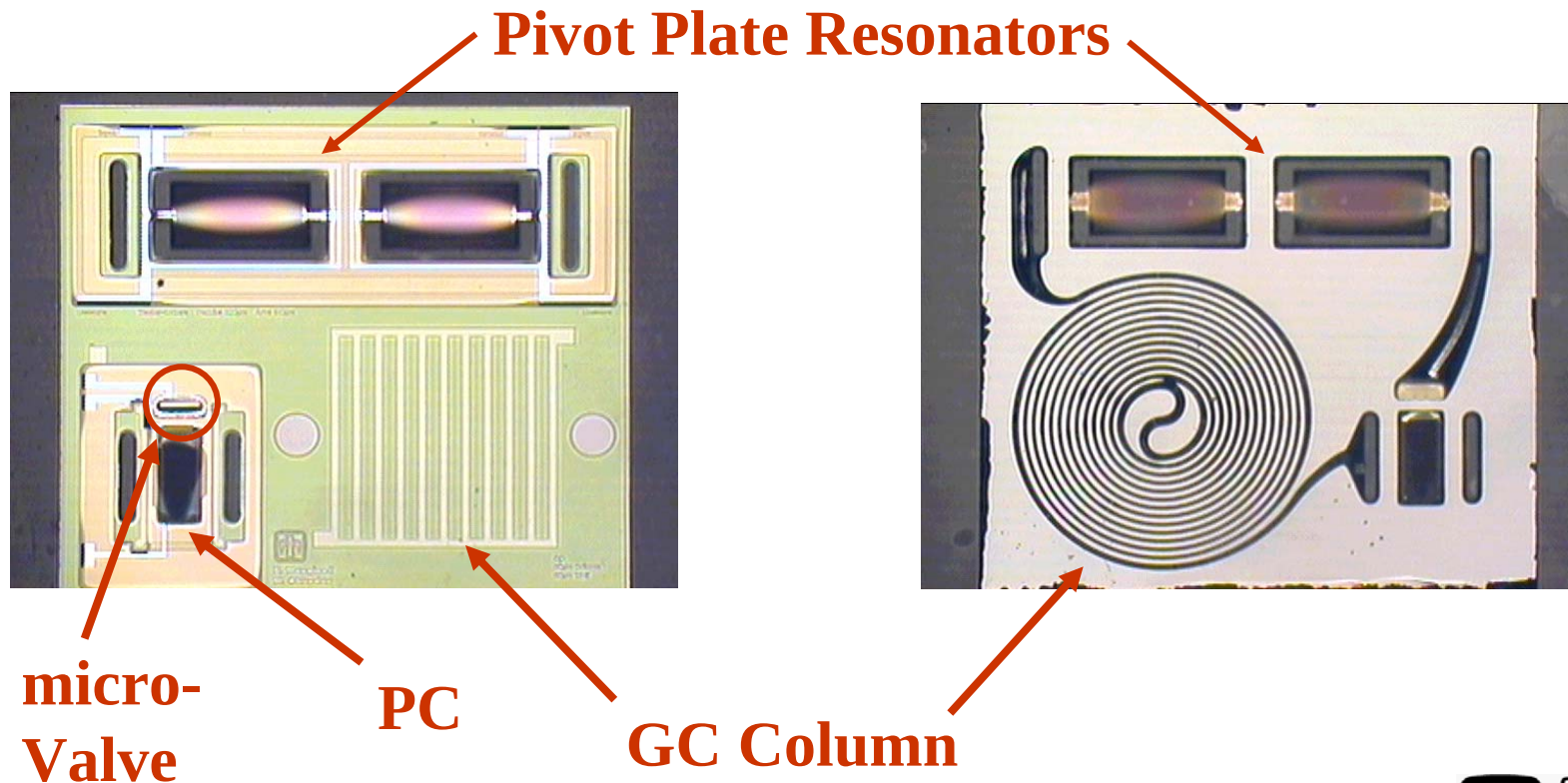
PPR – Pivot Plate Resonator



Integrated System with PPR

PC-GC-PPR System

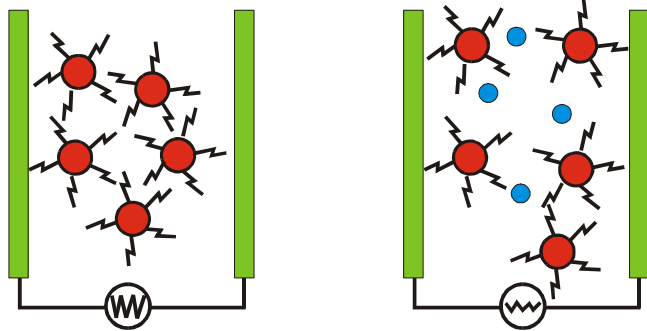
Goal: monolithic integration



PPR – Pivot Plate Resonator



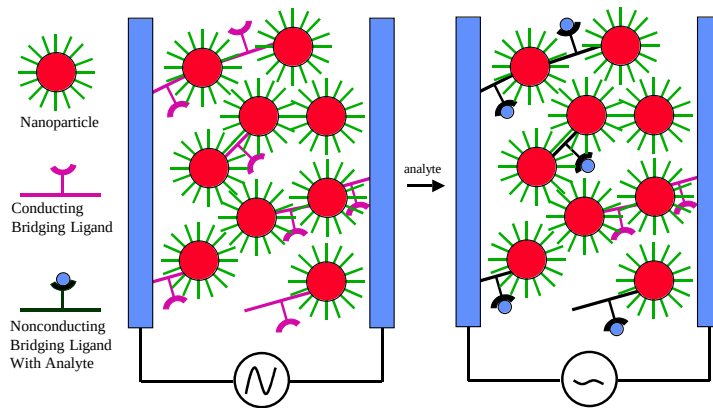
NanoParticle Ligand Bridge (NPLB) Detector



NanoParticle Chemical Resistors

Analyte absorbs in thin particle-loaded film. Film **swells** and separates particles reducing conductivity

Small Particle Array
Limited Number of Communication Paths



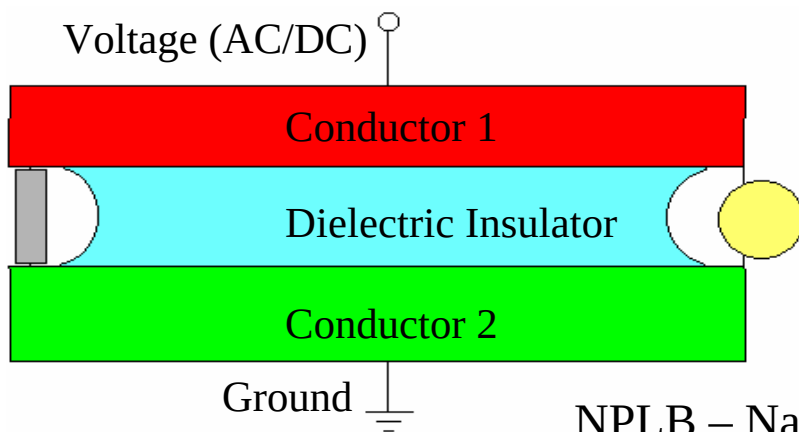
NPLB Detector

Analyte binding to pi-conjugated bridging ligand **reduces current flow** by perturbing the bridging ligand's conductivity.

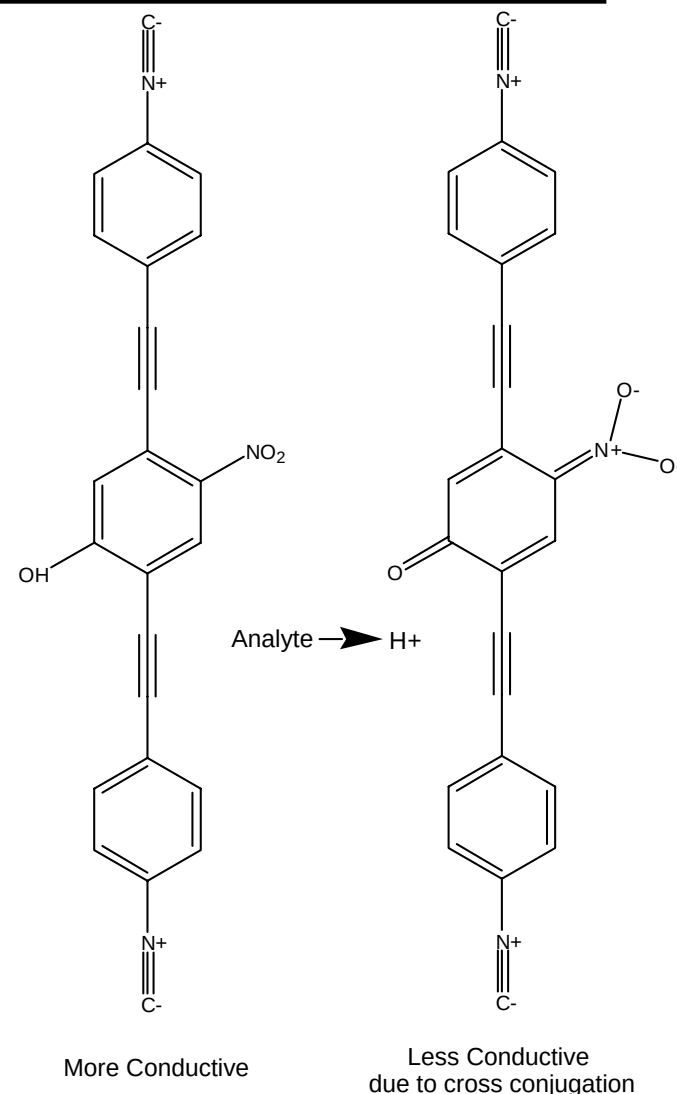
NPLB – Nano-Particle Ligand Bridge sensor

NPLB Construction

- Molecular wires control electronic communication between particles.
- Poly-nitro-phenol chains show high specificity for phosphonate groups
- Sulfur functionalizing end chains permits attachment to gold nanoparticles
- Difference in Homo/LumoGaps = 0.35 eV



NPLB – Nano-Particle Ligand Bridge sensor

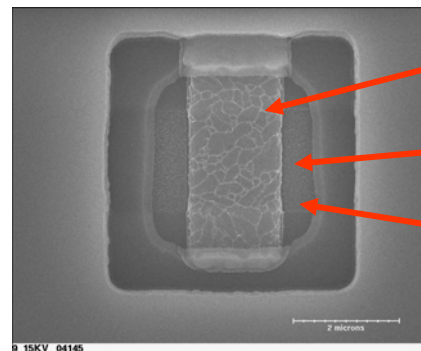
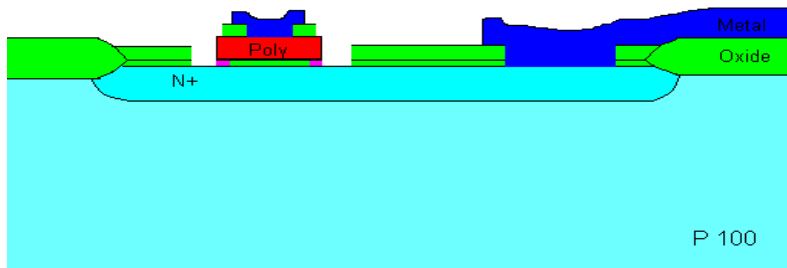




NPLB Construction

NPLB – Nano-Particle Ligand Bridge sensor

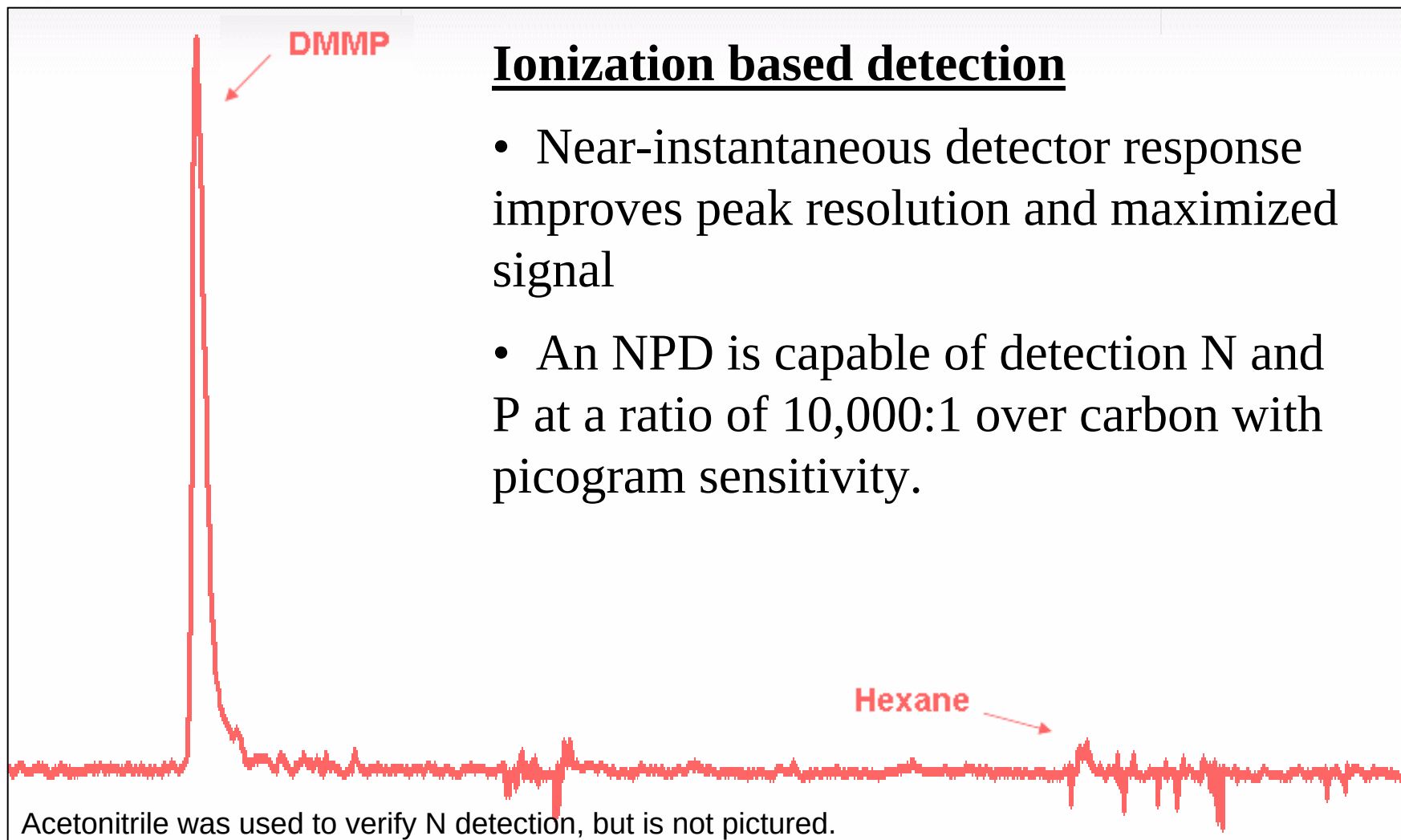
- Nanogap electrodes made through MEMS fabrication techniques
- Small ensemble of nanoparticles assembled between two nanoelectrodes -- particles migrate and structure under influence of an AC field.
- Ensemble stabilized by surfactant replacement -- weak bonds on nanoparticle replaced with tighter binding ligands (thiols or isocyanides)
- Limited percolation paths increases the sensitivity of the device. An ensemble with a large number of paths responds to a wider range of analyte concentrations before saturating.



poly-silicon
NPLB in gap
(+) semi-conductor



Nitrogen-Phosphorous Detector

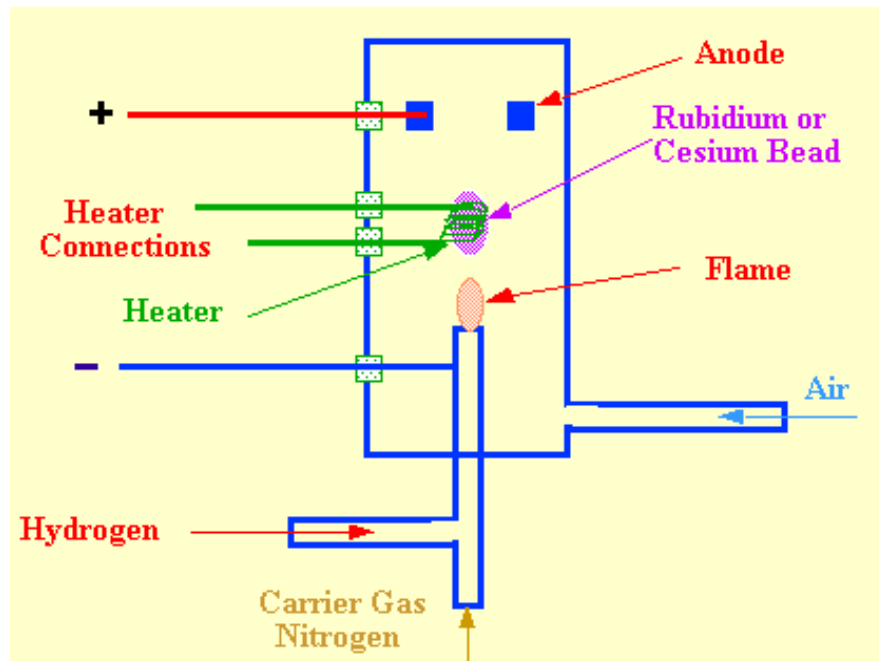


NPD – Nitrogen Phosphorus Detector



Sandia's Micro-NPD

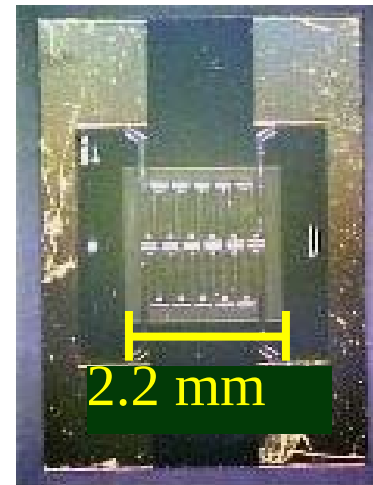
Commercial NPD



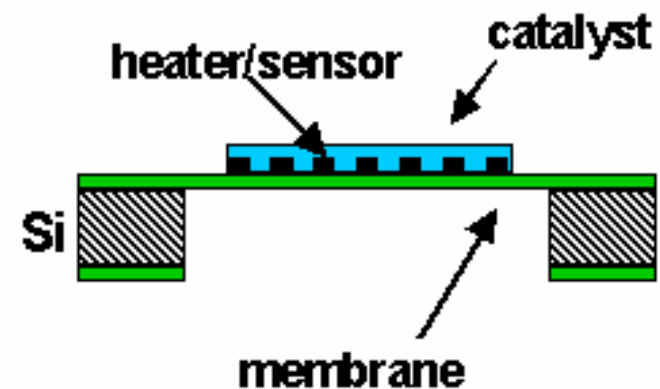
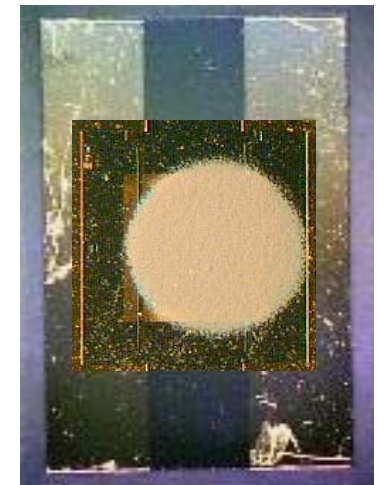
Sandia's micro-NPD has equivalent selectivity as commercial NPDs in a much smaller package. Electrodes will eventually exist on planar substrate.

NPD – Nitrogen Phosphorus Detector

Uncoated

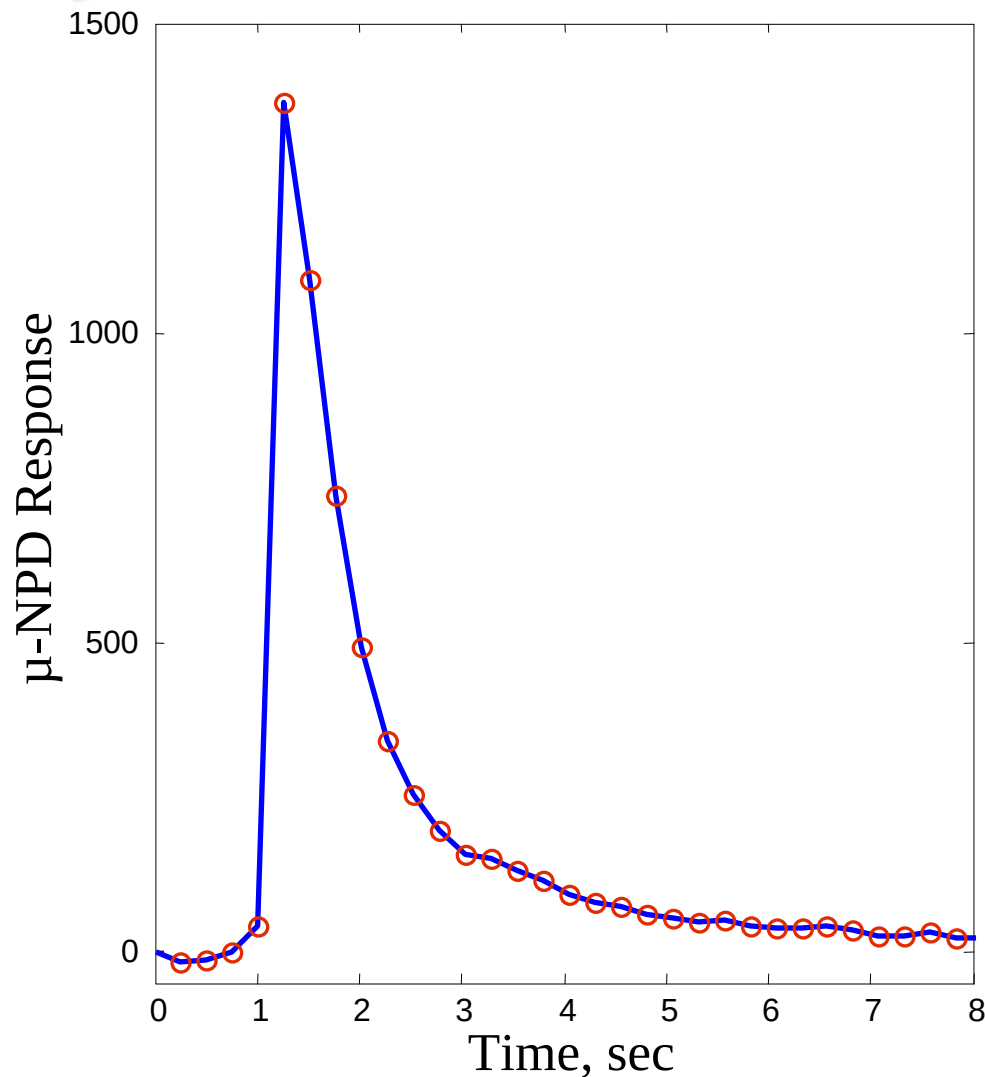


Coated





μ ChemLab with μ NPD



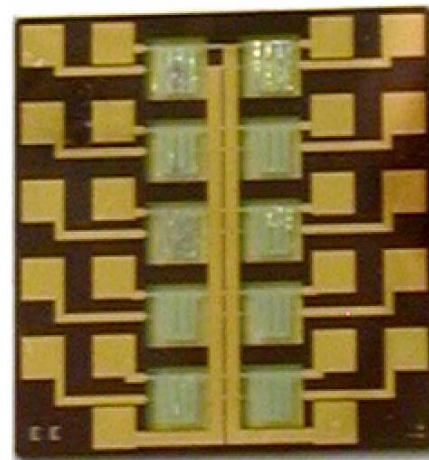
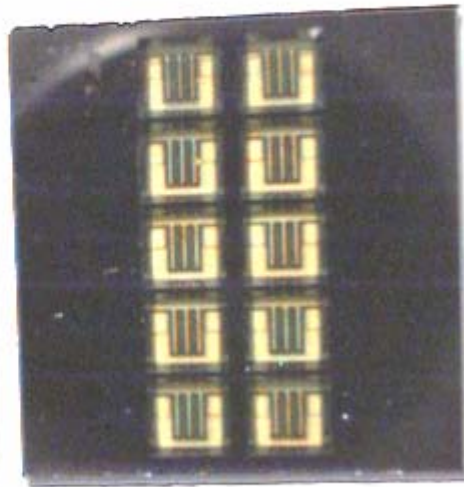
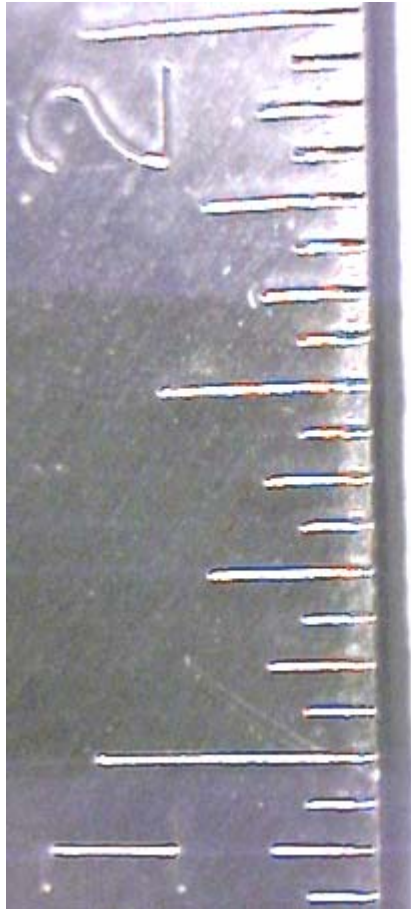
NPD – Nitrogen Phosphorus Detector

- μ NPD and SAW sensors in μ ChemLab
- Low-level nitrated hydrocarbon analyte collected for 60 seconds
- PC decomposes analyte upon thermal desorption
- μ NPD shows excellent response to resulting NO_x products.
- 4 Hz DAQ rate too slow (may have missed peak)



Micro-Calibration Chip

- **10 Element Calibration Array** for retention time and sensor response
- Thin silicon nitride membrane (1 micron)
- Thermally labile chemical placed on each membrane
- Patterned metal heating element flash decomposes the chemical, injecting products into the GC column

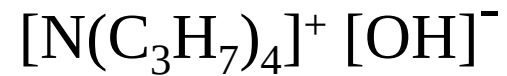


Micro-Calibration Chip

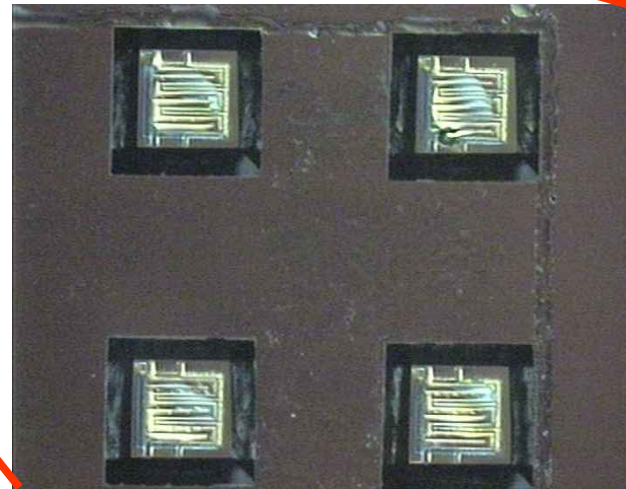
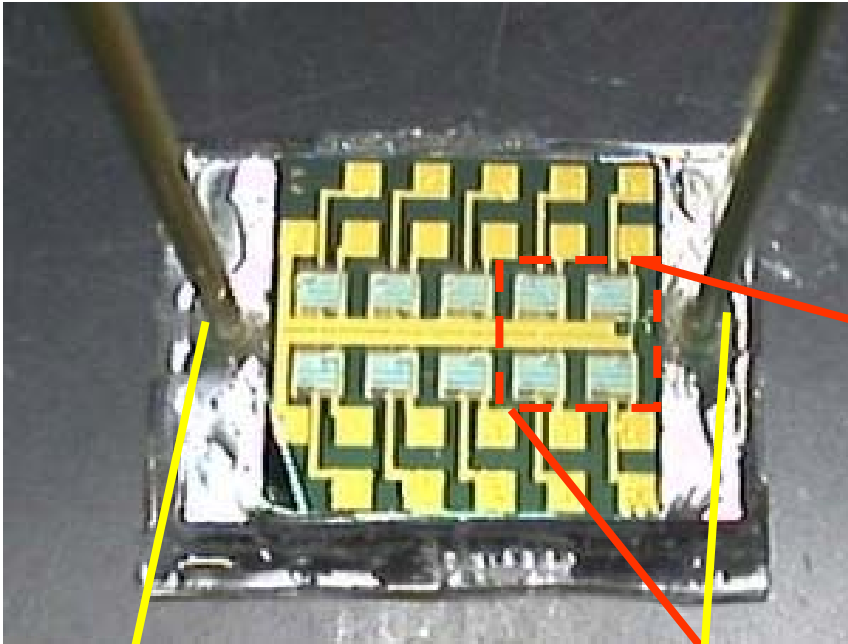
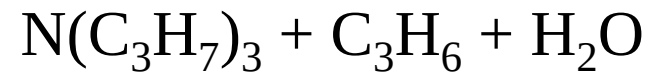


Construction/Coating

tetrapropyl ammonium hydroxide



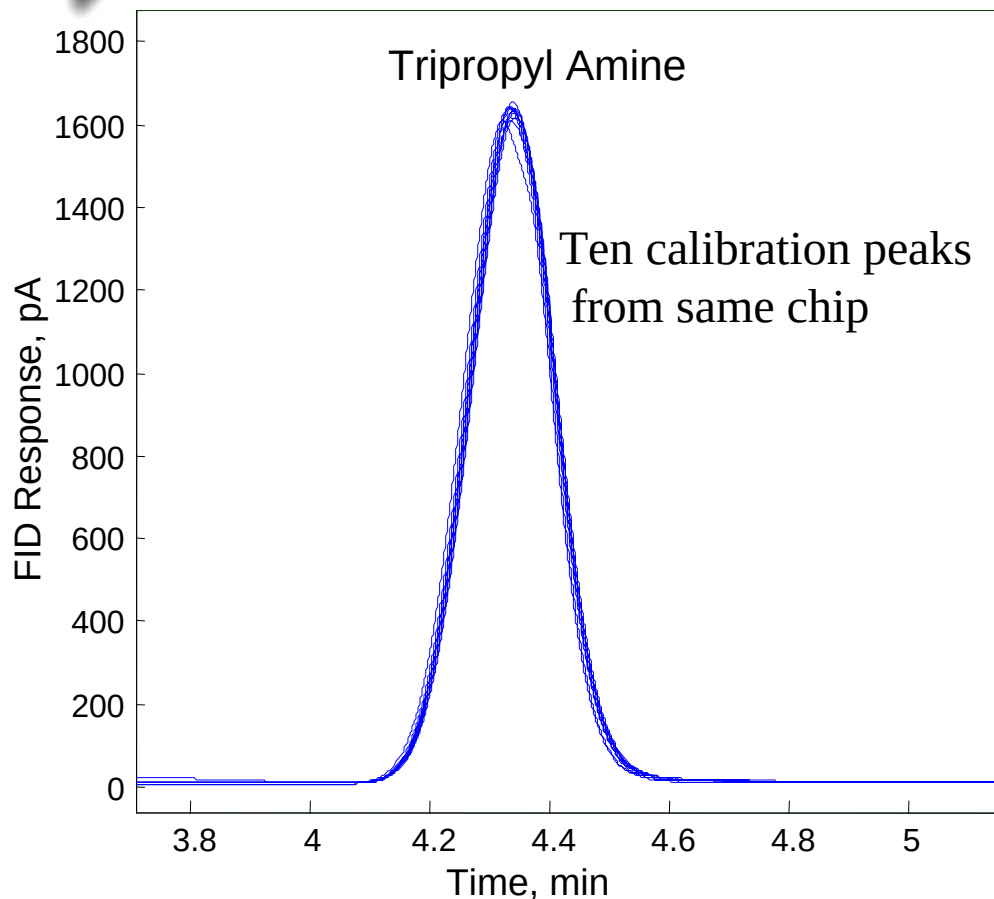
tripropyl amine + propene + water



Micro-Calibration Chip



Micro-Calibration Chip



Fluidic fixturing pieces were HMDS treated prior to fixture assembly. Air carrier at 7 p.s.i., flow rate 11 ccm, oven 60C, 15-m DB-1 megabore column, FID.

Reproducibility (one chip)

- Mass flux: 0.5%
- Peak height: 1.0%
- Peak Width: 1.3%
- Retention Time: 0.14%

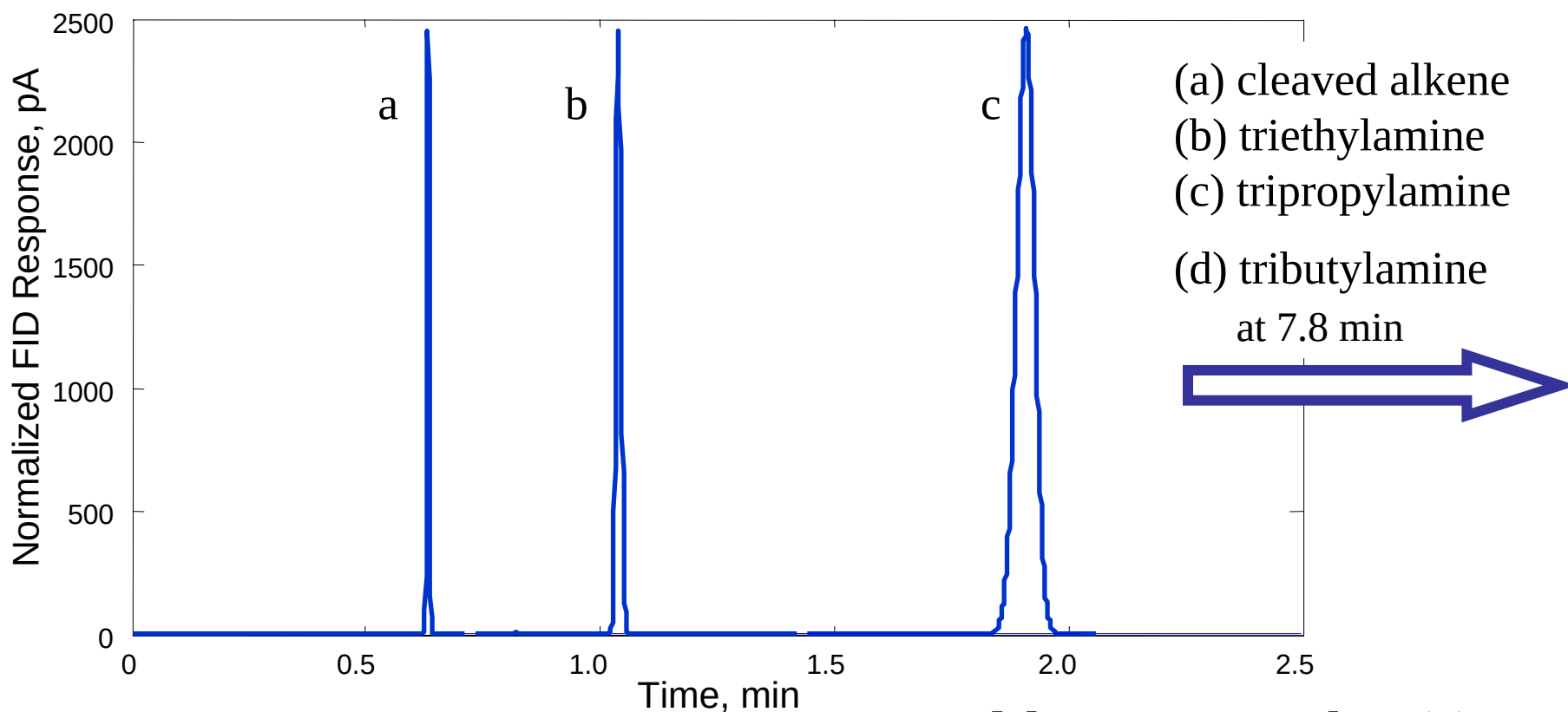
Reproducibility (between chips)

- Mass flux: 5%
- Peak height: 5.5%
- Peak Width: 0.06%
- Retention Time: 0.8%

Micro-Calibration Chip



Calibration Markers



Air carrier at 5 p.s.i., flow rate 11 ccm, oven 100°C,
15-m DB-1 megabore column, FID.

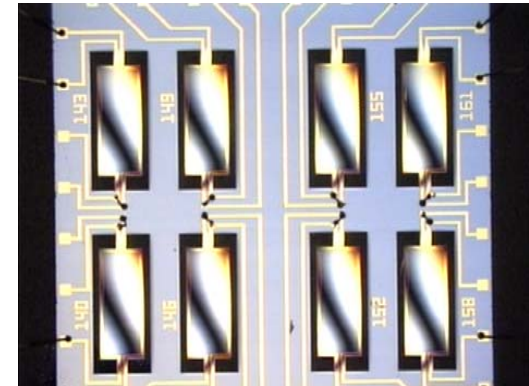
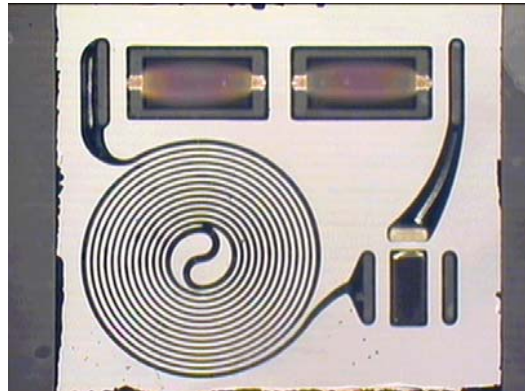
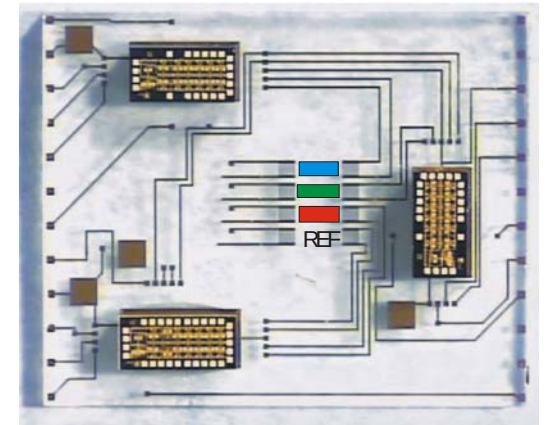
- Calibration marker(s) chosen to best match analytical task.

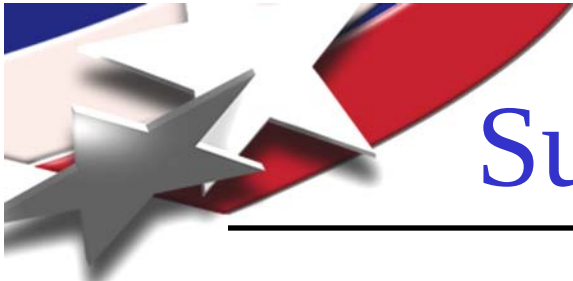
Micro-Calibration Chip



Summary and Conclusions

- Basic micro-ChemLab uses preconcentration, separation and detection stages
- Currently we use a hybrid integration of these stages
- Ultimate goal is to integrate these stages on a single substrate
- New sensor technologies will allow this full integration





Summary and Conclusions

Desired Features for Future Detectors

- Monolithic integration – low cost, rapid production, no assembly
- Simple operation – simple electronics, little/no post-fabrication steps
- Low power – long life in field portable applications
- Rapid response – higher chromatographic resolution
- Low noise and high sensitivity (picograms)
- Arrayed response – better analyte discrimination, low false-alert

Sensors Under Investigation – Operating Mechanism

- Pivot Plate Resonator (PPR) – microbalance
- Nano-Particle Ligand Bridge (NPLB) – electrical conductivity
- Nitrogen Phosphorous Detector (NPD) – thermionic ionization

Also: Microcalibration device for GC and sensor calibration



Behind the Scenes

Acknowledgements

Steven Showalter – NPD coatings

Jim Barnett – NPD device testing

James Sanchez – general microfabrication

Joseph Bauer – PPR integration and microfabrication

Jennifer Ellison – microcalibration device testing

John Dickenson – PPR testing and software



PPR Theory

$$J \ddot{\Theta} + C_t \dot{\Theta} + k \Theta = \mathbf{T},$$

$$\mathbf{T} = T \exp(j\omega t) = B w L I \exp(j\omega t) = B w L \mathbf{I},$$

$$J = \rho w c L (c^2 + L^2)/12$$

$$k = 2 \beta b c^3 G / a, \quad \beta = f(b/c) \approx 1/3$$

$$C_t = \text{damping coef.} = \sqrt{k J} / Q = 2 \zeta \sqrt{k J}$$

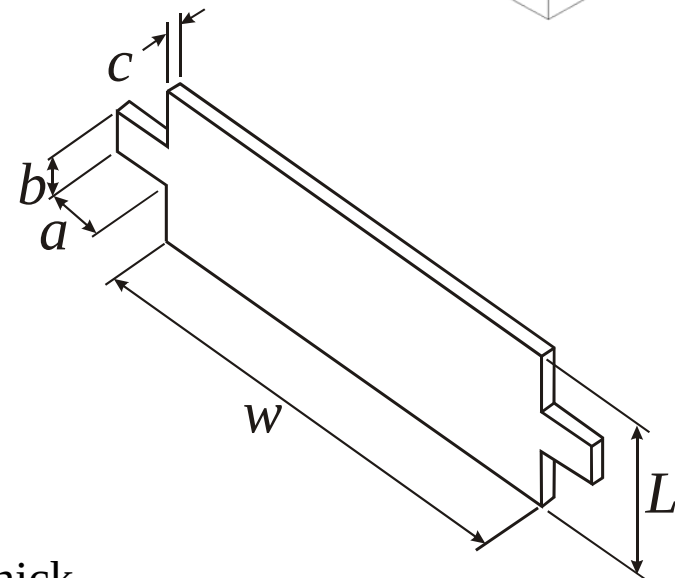
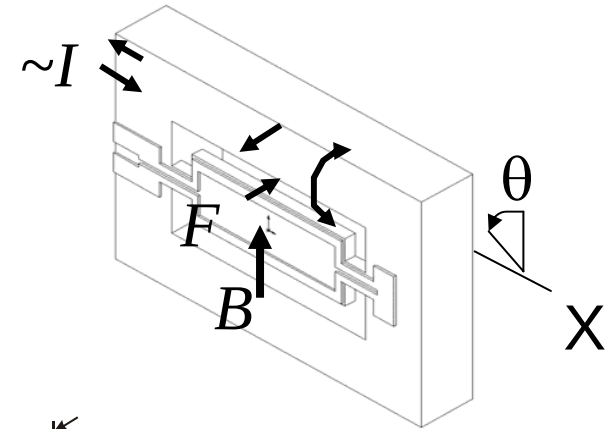
solution:

$$\omega_n = \sqrt{k/J} = \sqrt{\frac{8 b c^2 G}{\rho w a L (c^2 + L^2)}},$$

$$r = \frac{\omega}{\omega_n},$$

$$\mathbf{Z} = \frac{\mathbf{V}}{\mathbf{I}} = R_0 - \frac{B w L j \omega \bar{\Theta}}{I} = R_0 + \frac{j \omega (B w L)^2 / k}{1 - r^2 + 2 r \zeta j}$$

$$= |\mathbf{Z}| \exp(+j\phi_Z)$$



Typical Paddle: 1500μm wide x 600μm tall x 10μm thick

Typical Tab: a = 200μm; b = 160μm; c = 10μm Resonant Frequency = 26kHz