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Micro-Flame Ionization Detection Using a Catalytic Micro-Combustor

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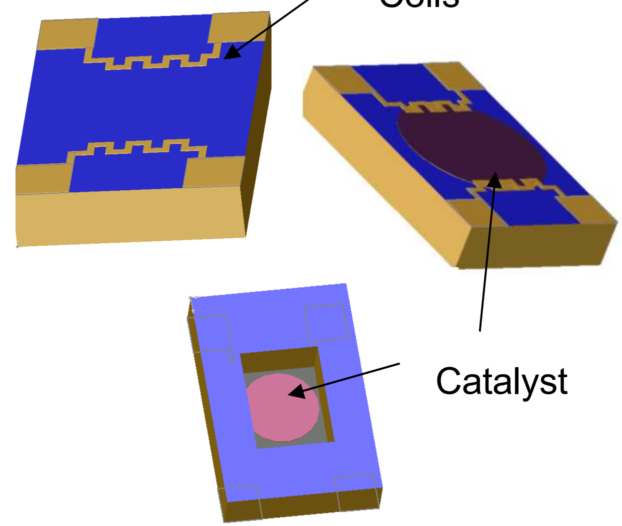
Outline



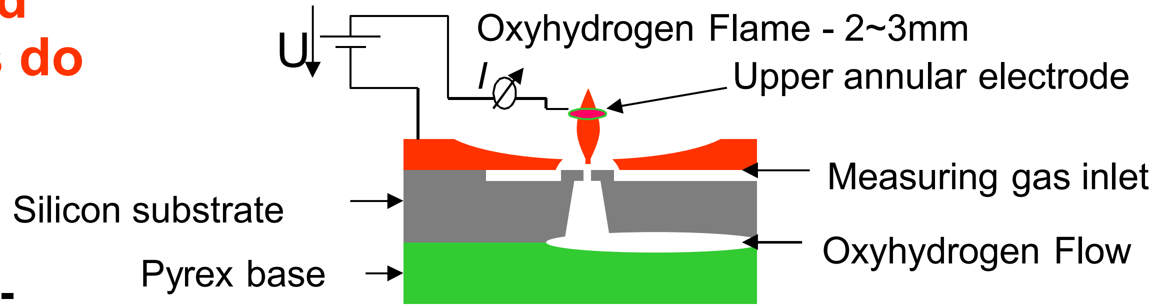
- Micro-combustor theory
  - Micro-flame vs. catalytic combustion
  - Calorimeter and fixture components
    - Design and fabrication
  - Analyte ionization and electrometer detection
- Analyte signatures
  - Calorimeter discrimination of analytes
  - Synchronized electrometer and calorimeter detection to reduce false positives
- Results
  - Bias vs. Signal
  - Flow vs. Signal an optimization study
- Conclusion

Motivation

- **Area's of interest:**
  - **Need for fast, sensitive detectors that aren't sorption based**
  - **Selectivity through arrays of cross-sensitive detectors and inherent selectivity in some array elements (e.g., FID)**
  - **Low power, small for portability**
- **Impact:**
  - **Very large potential impact in hand-held detection for chem-bio, petrochemical, sulfur in fuels, pesticides…**

Micro-flame vs. Micro-combustor

- **Conventional flames and high-temperature beads do not scale well for minaturization and portability**
  - **Increased surface-area-to-volume prohibits flames**
  - **Power consumption minimization is required**
- **Approach: use a low heat capacity, low conductance membrane**
  - **1 micron thick membrane, 10^{-6} J/K, 1.5 W/mK**
  - **Thin film heater and sensor film (e.g.,10% - Pt/Alumina)**
  - **500°C in 20 msec, 300 mW**



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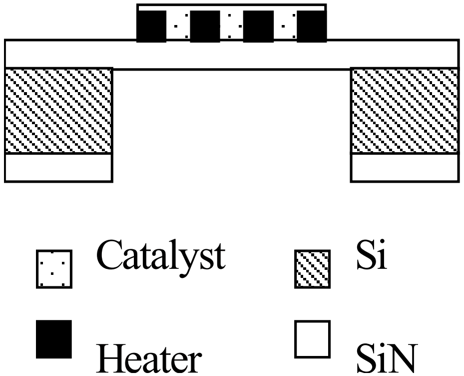
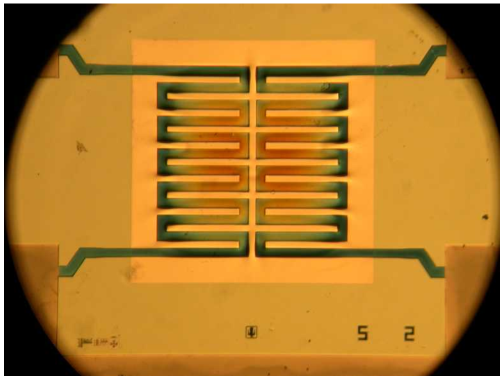


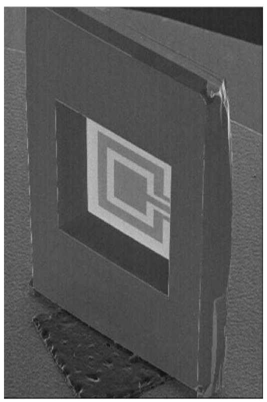
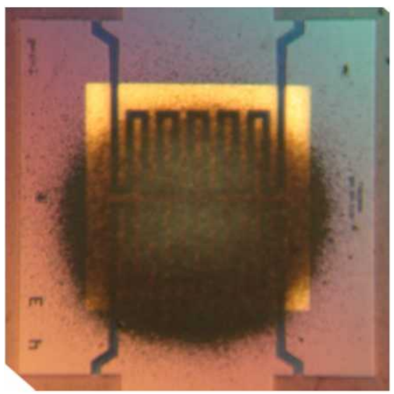
Cross sectional Schematic of micro-combustor design.



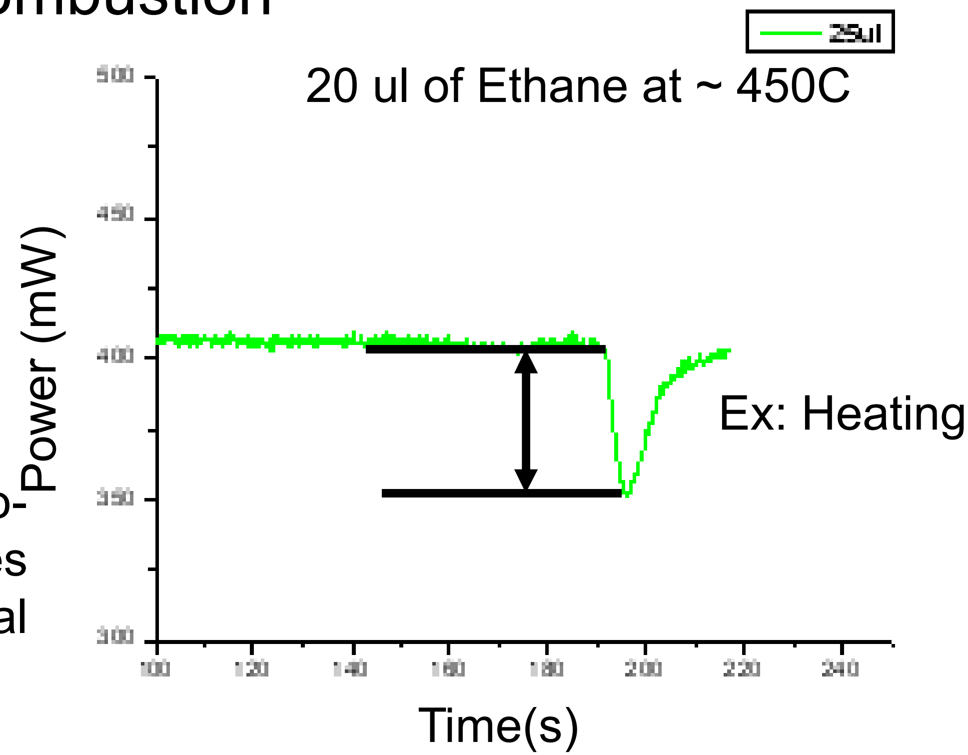
Describing Hot plate wiring after usage. Current tracing is established.

Calorimeter signatures

- Measuring varying quantities of evolved heat
  - Example: Ethane combustion

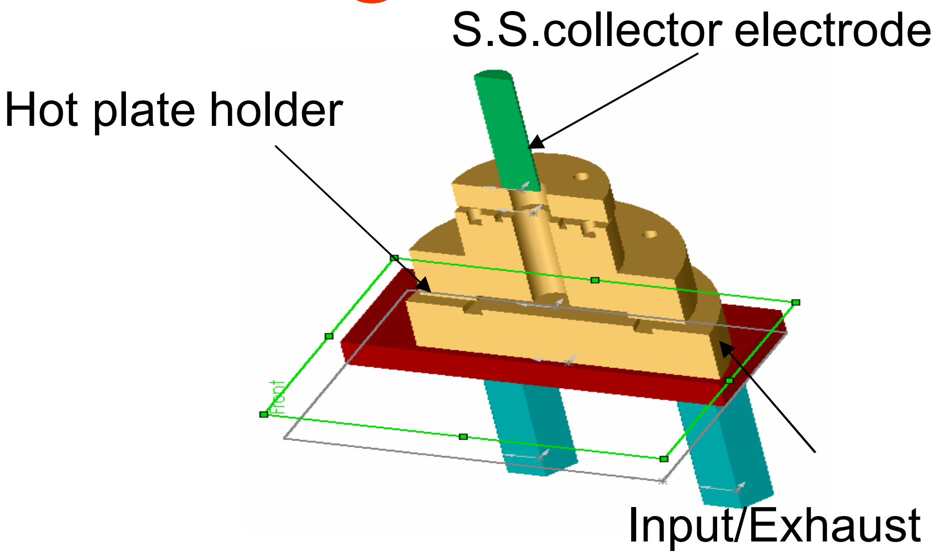



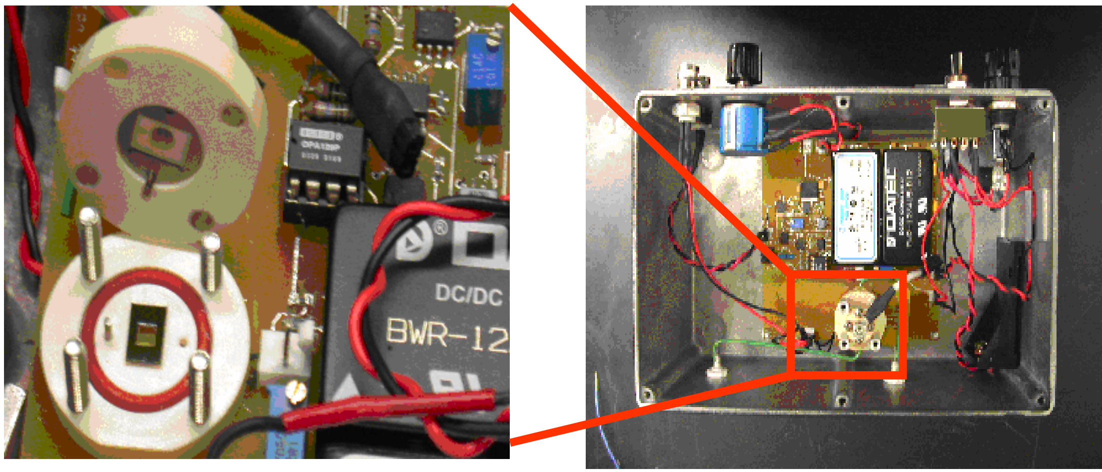
Spray coated ~ 10% Pt/Alumina. Micro-combustor burn in procedure removes oxidation of alumina to revitalize optimal calorimeter operation.



Micro-FID Design

- **Design Considerations**
  - Minimal volume to maximize analyte response during combustion.
  - Heated to reduce water formation from combustion by-products.
  - Commercial column used to reduce pressure pulse from injector valve.
  - Proportionally mixed gas input – Air,H_2 and N_2 to optimize burn and signal.
  - Collector bias is essential to maximize response.





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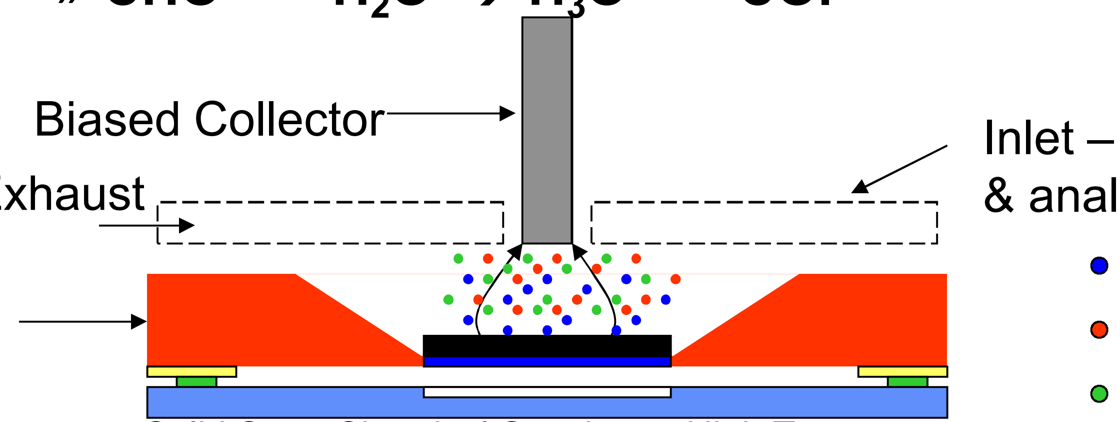
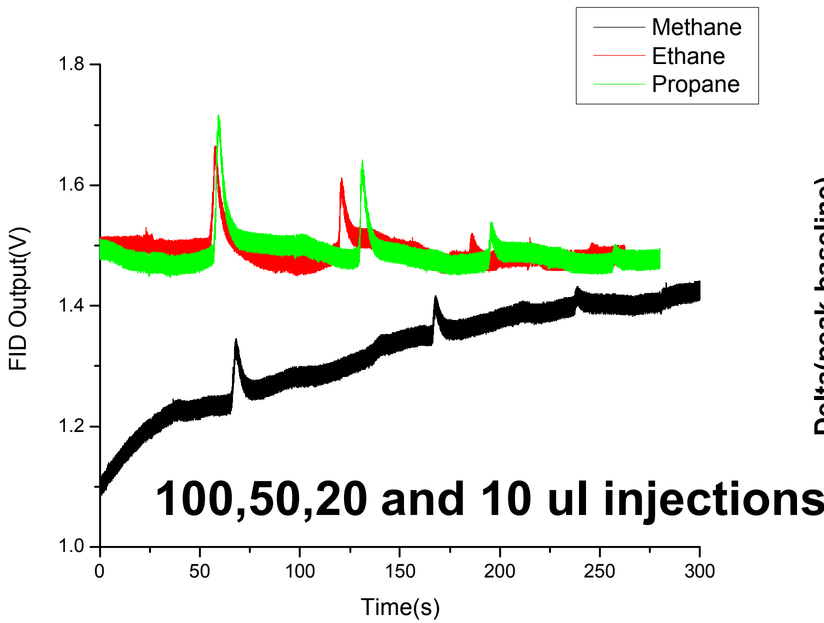
Analyte Ionization

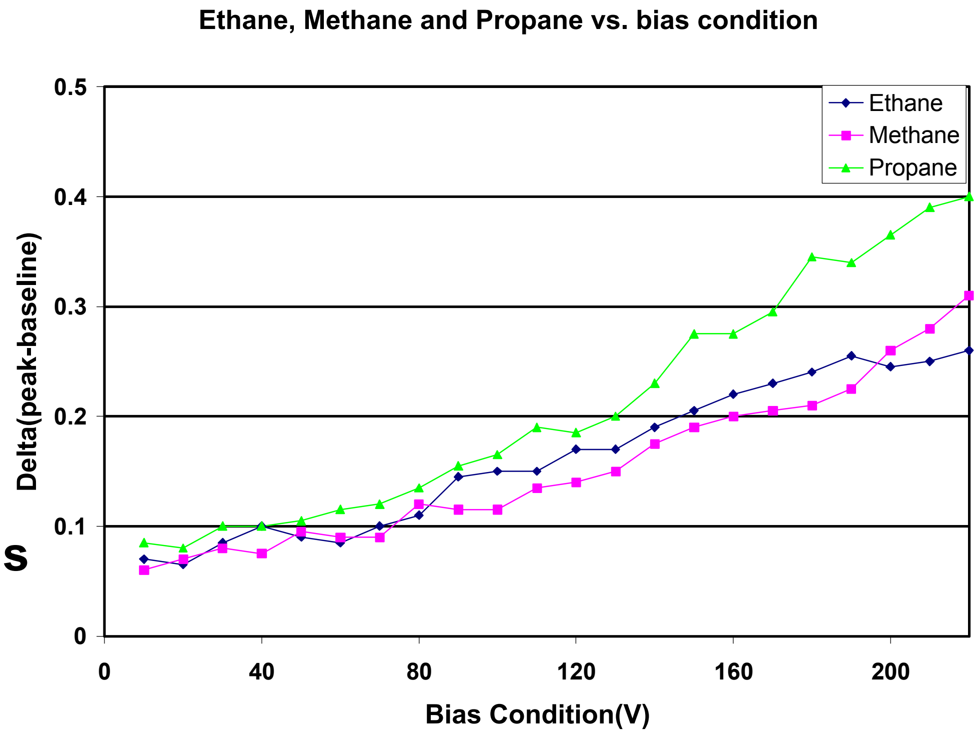
- Ion production from hydrocarbons in flames is primarily the result of chemi-ionization of CHO* :
  - » $CH + O \rightarrow CHO^* \rightarrow CHO^+ + e^-$. (1)
- The formylium ion, CHO+, reacts quickly with water produced in the flame to produce hydroxonium ions (H3O+), the primary charge carrying species responsible for the ultimate FID response .
  - » $CHO^+ + H_2O \rightarrow H_3O^+ + CO.$ (2)



Bias vs. Signal

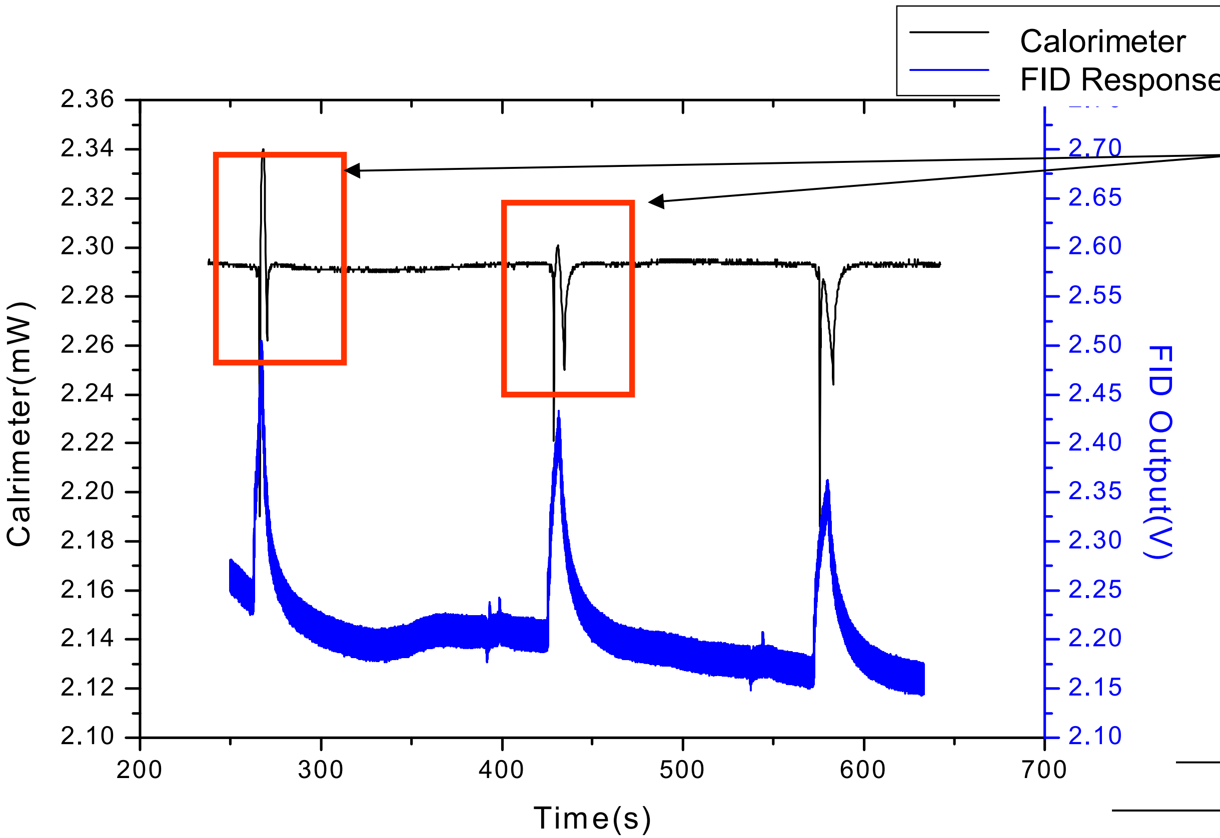
- Ethane, methane and propane





Dual mode operation

Functionality of calorimeter and electrometer usage for real time analysis.

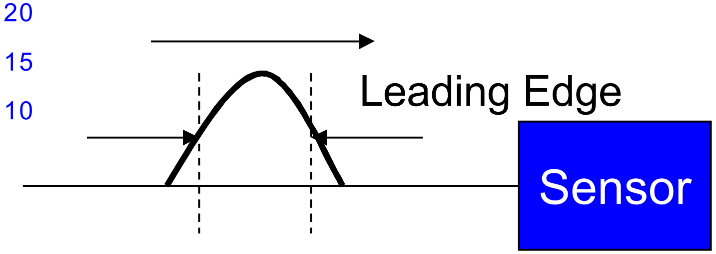


Unstable burn conditions

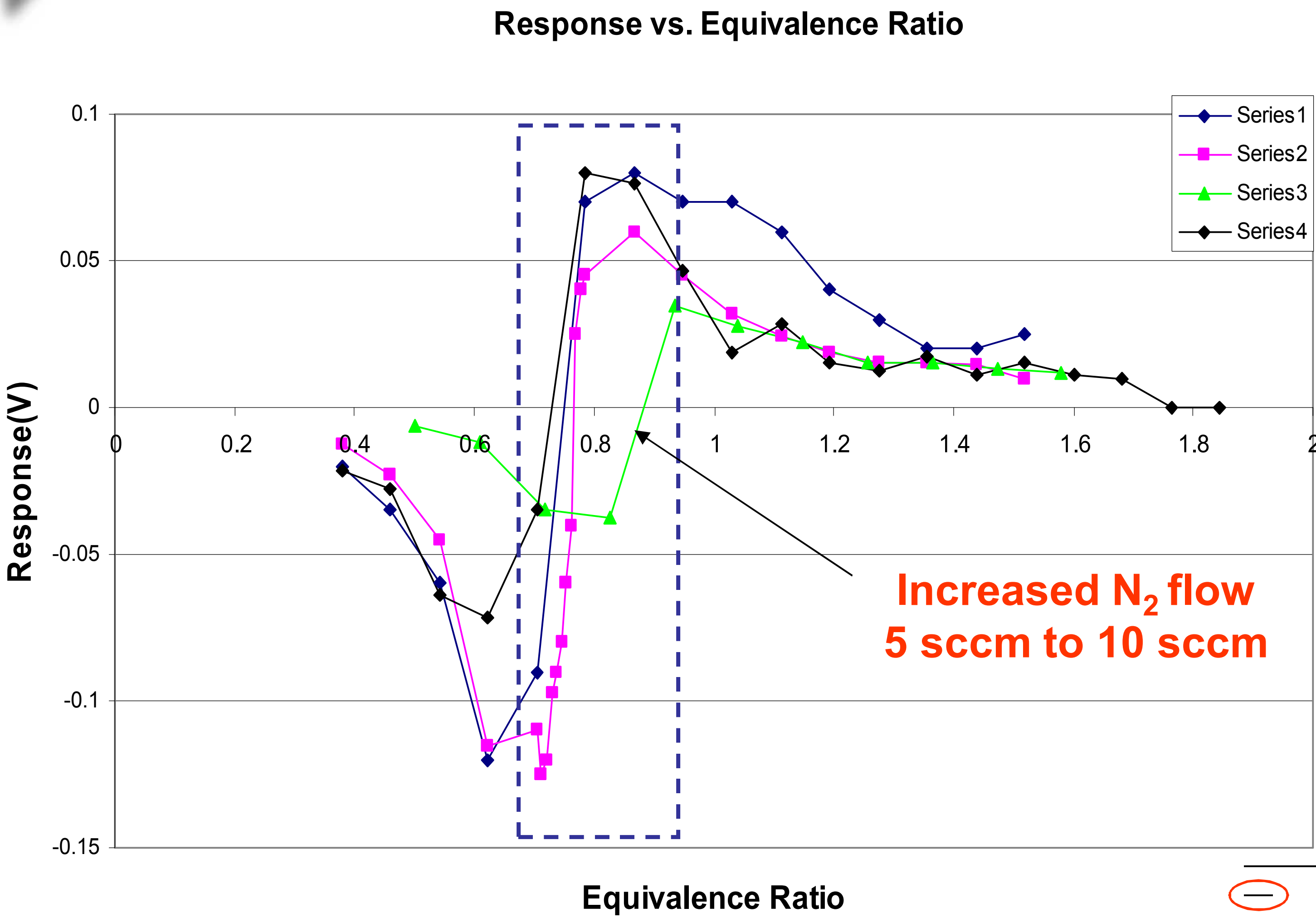
Potential reasons:

1.) Lean/Rich/Lean fuel mixture.

2.) Causes pos./neg./pos. response.



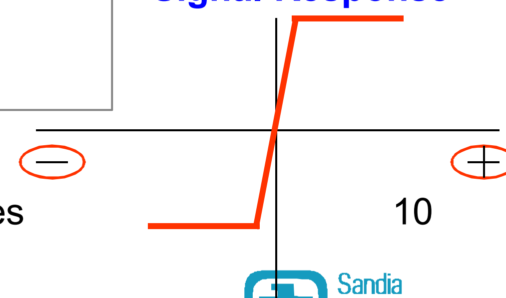
FID Response vs. Equivalence Ratio



Stoichiometric:
~28% H_2 = 1

Inflection point = ~0.8 creating a positive and negative response to occur at a lean fuel mixture.

Signal Response



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Mechanism of ion production and collection

- Verified signal polarity with pico-amp meter source.
  - 10 pA – 100pA equated to our signal levels.
- Surface vs. gas phase reaction point
  - Point at which the flame becomes lifted off the catalyst surface.
- Influence of nitrogen on FID response
  - FID response is insensitive to pure nitrogen flow
  - Shifts inflection point and magnitude
- Gas phase electrochemistry
  - No circuit interference with signal (not connected)
- Temperature effects
  - Temp. of fuel/air flame is convoluted w/ ion signal

Conclusion

- A low power field portable micro-combustor has been demonstrated using single and dual mode detection for unique organic signatures.
- Ruled out interaction between calorimetric operation influencing electrometer signal.
- Flow rates influencing small volume gas phase combustion kinetics are still being investigated.
- Determining thermal/ionization activities on electrometer circuitry.

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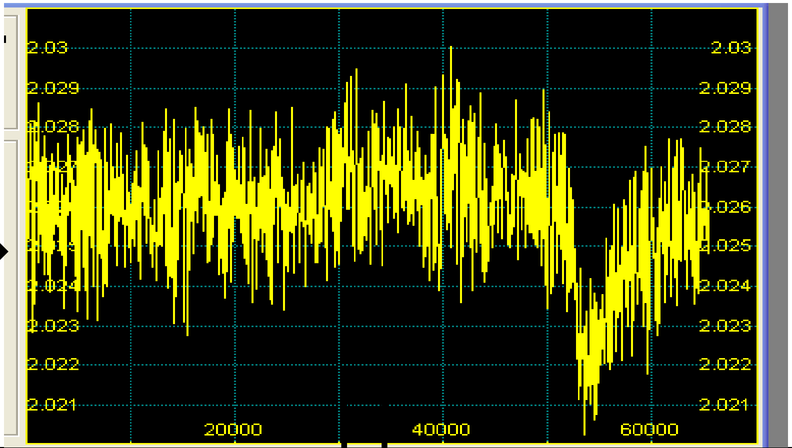
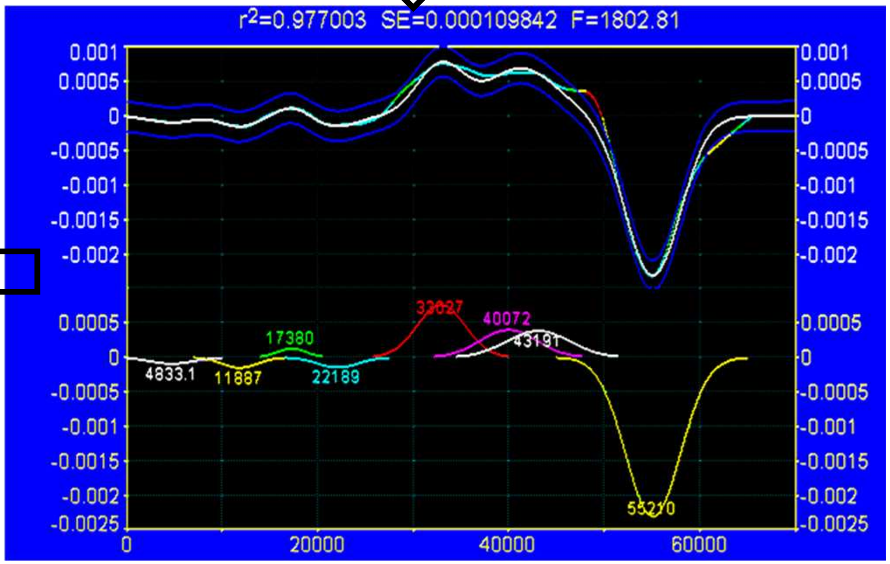
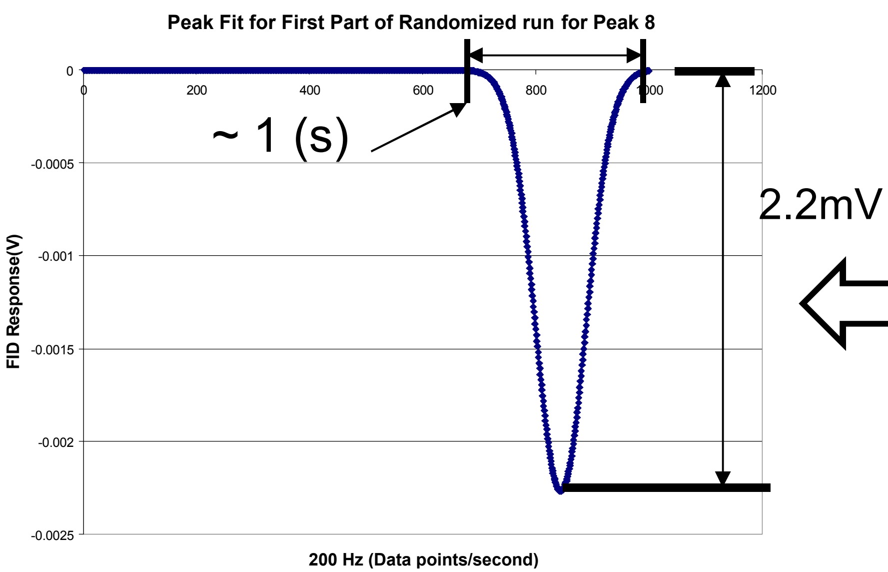
Peak Fitting

- Raw Data filtering due to background combustion noise.
- ~16% Loess smoothing function
- Baseline subtraction
- Gaussian Area calculation w/ FHWM
- ~97% R^2







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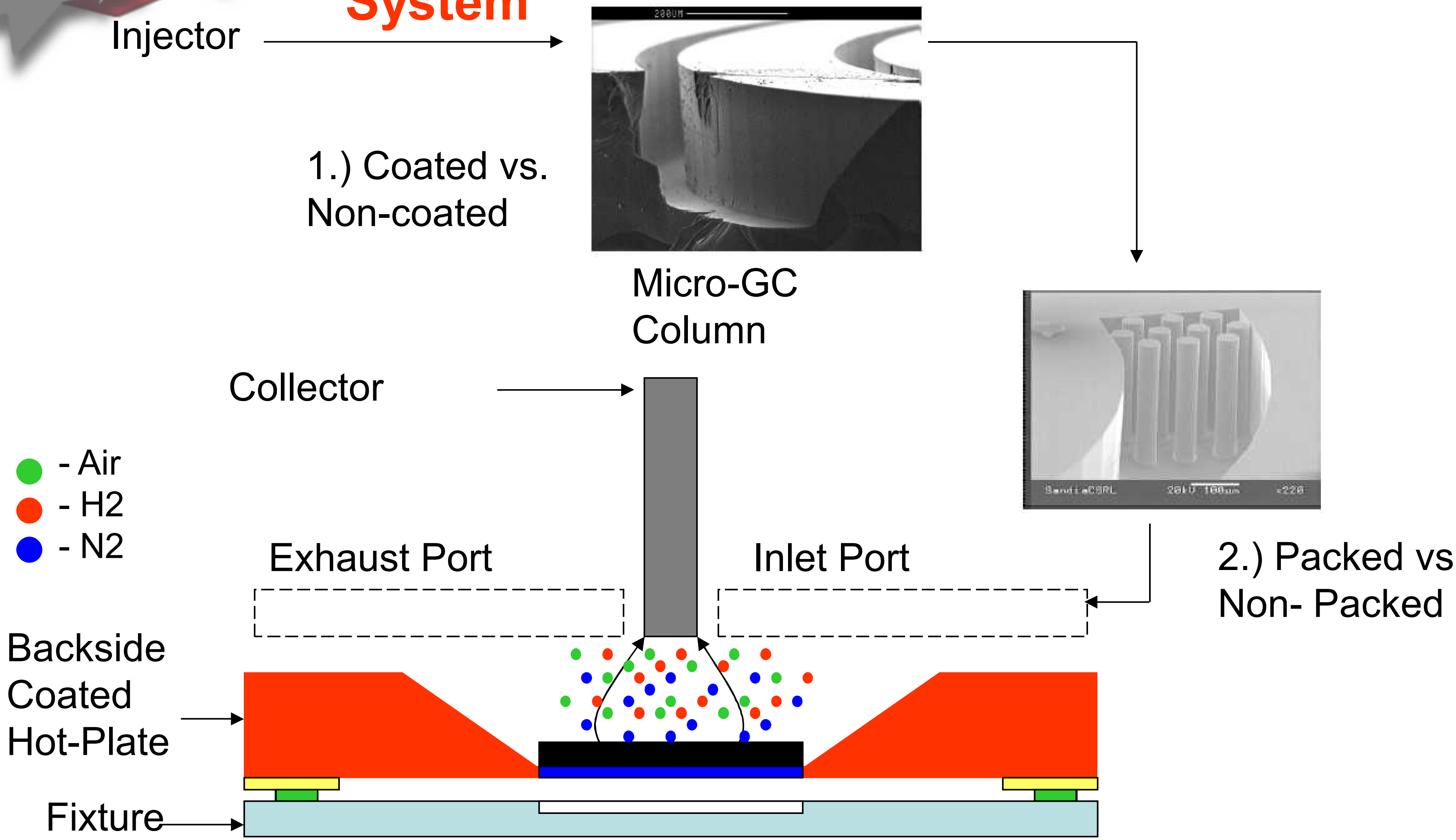
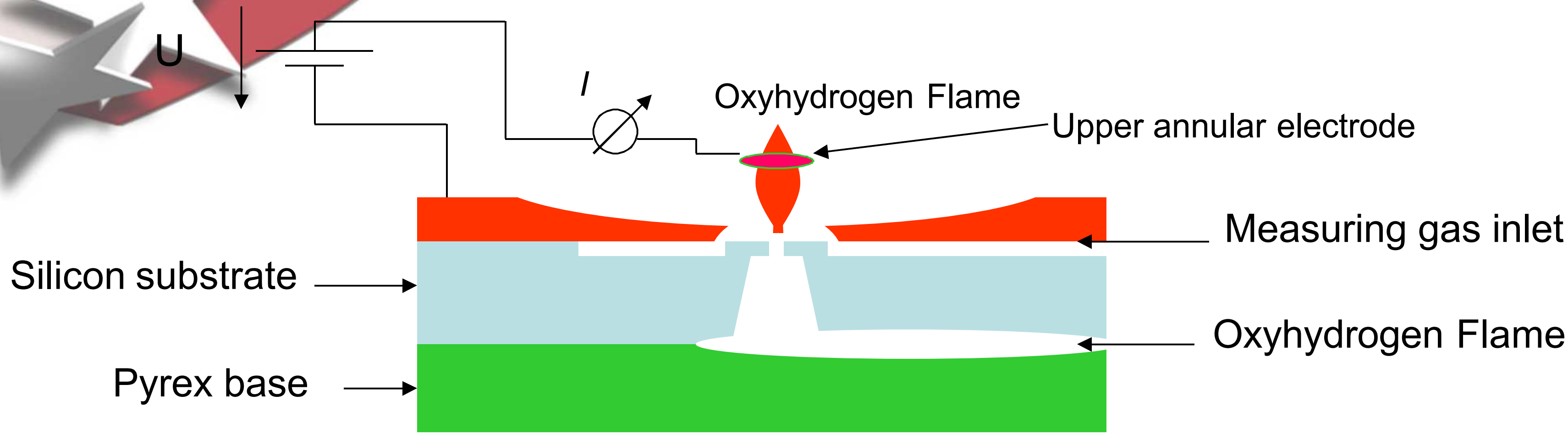
Future Micro-combuster/ionization System



Additional Considerations

- Similarities to commercial FID's.
  - Analyte signal magnitude and repeatability
- Liquid vs. Headspace
  - The conversion of liquid to vapor opposed to entering at a vapor phase.
- Carrier vs. Non-carrier gas injection.
  - No flame to stabilize due to catalyst.
  - Elevated Hot-plate temperatures can cause combustion and collection of Analyte. H_2?



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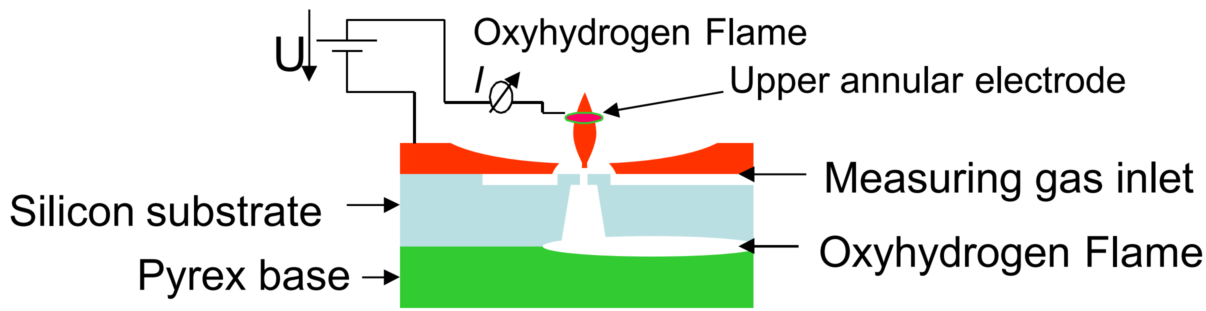

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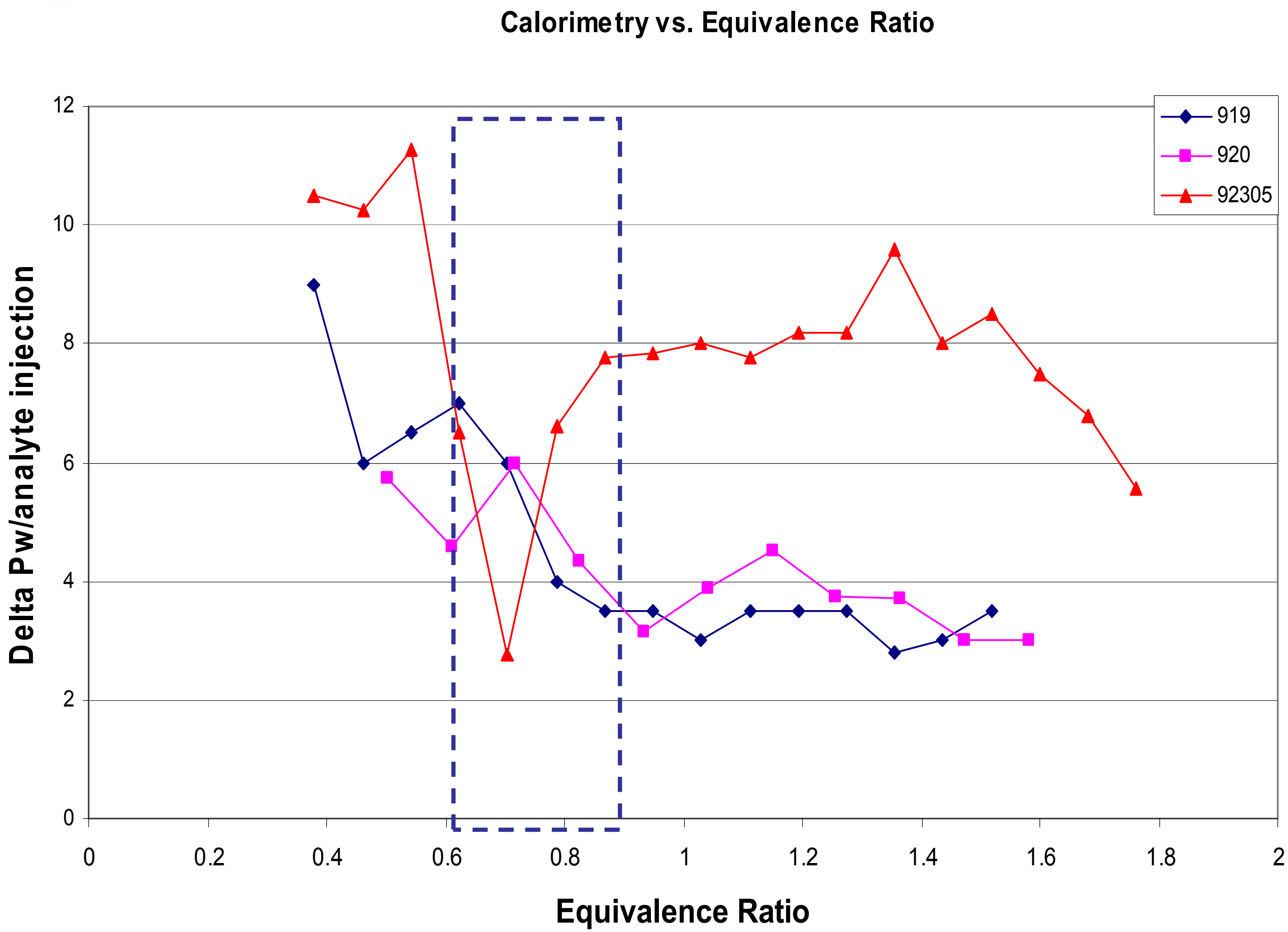
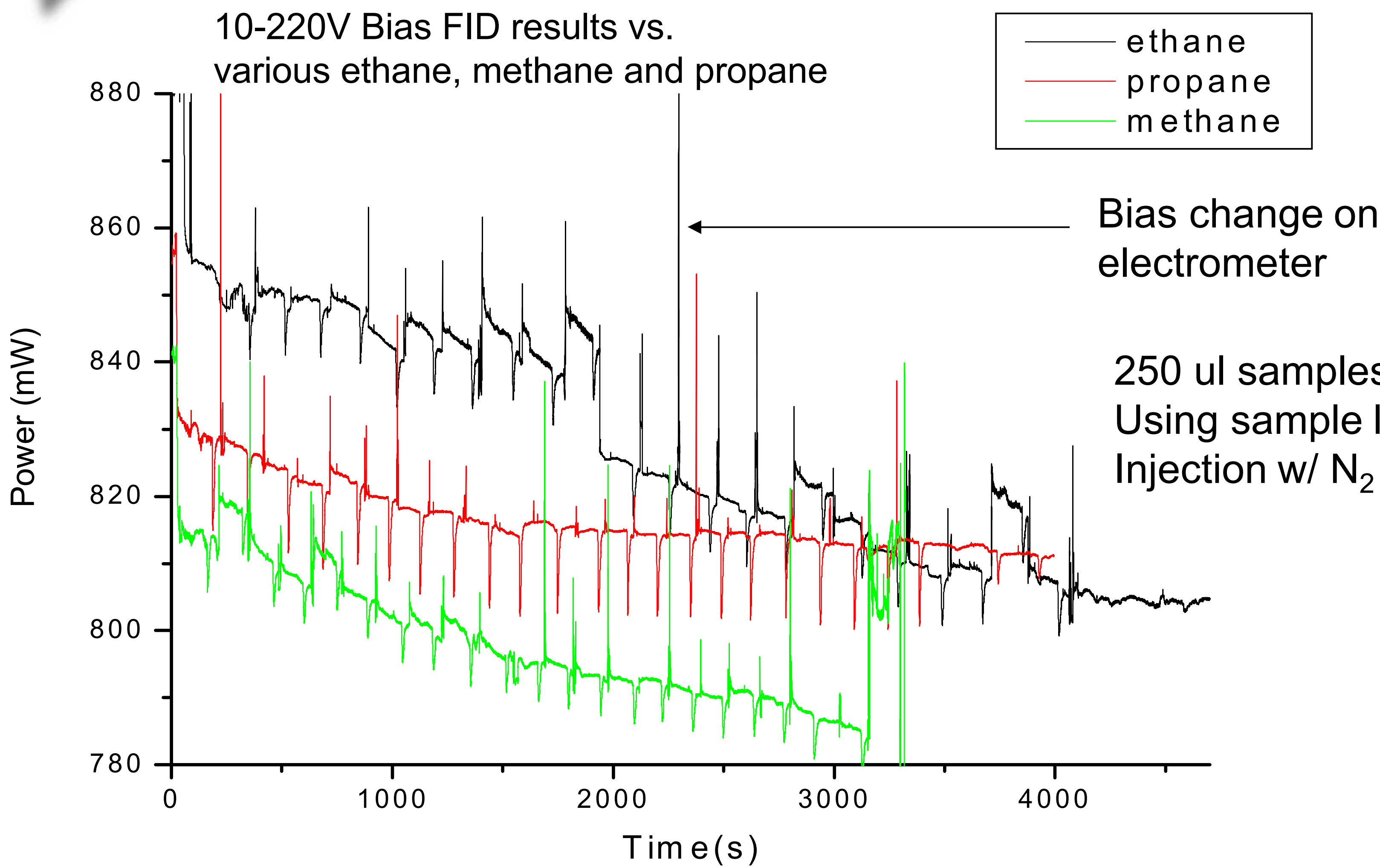
Calorimeter response vs. Equivalence Ratio



Equivalence Ratio Calculation:

$$\frac{H_2 \text{ flow}^*(2.016)}{\text{Air flow}^*(28.84)} {}^*(34.3)$$

Calorimeter Detection



250 ul samples
Using sample loop
Injection w/ N_2 as carrier