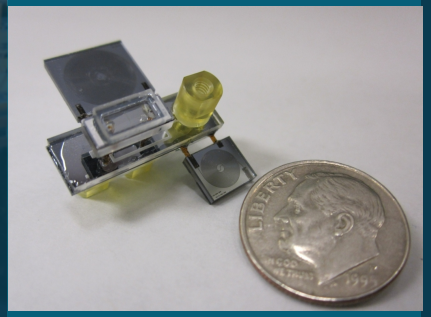
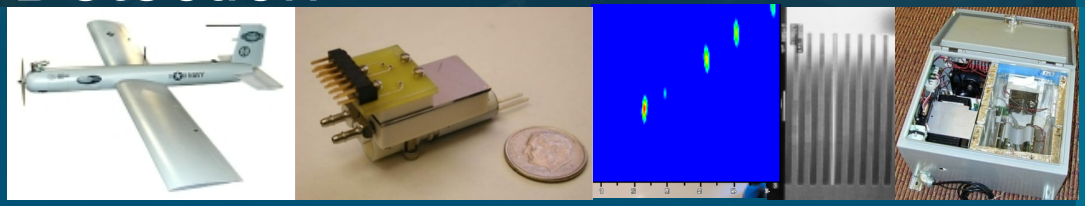
SAND2019-7645PE

Sandia National Laboratories

µChemLab™ – Twenty Years of Developing Microfabricated Gas Analyzer for Chemical Detection





PRESENTED BY

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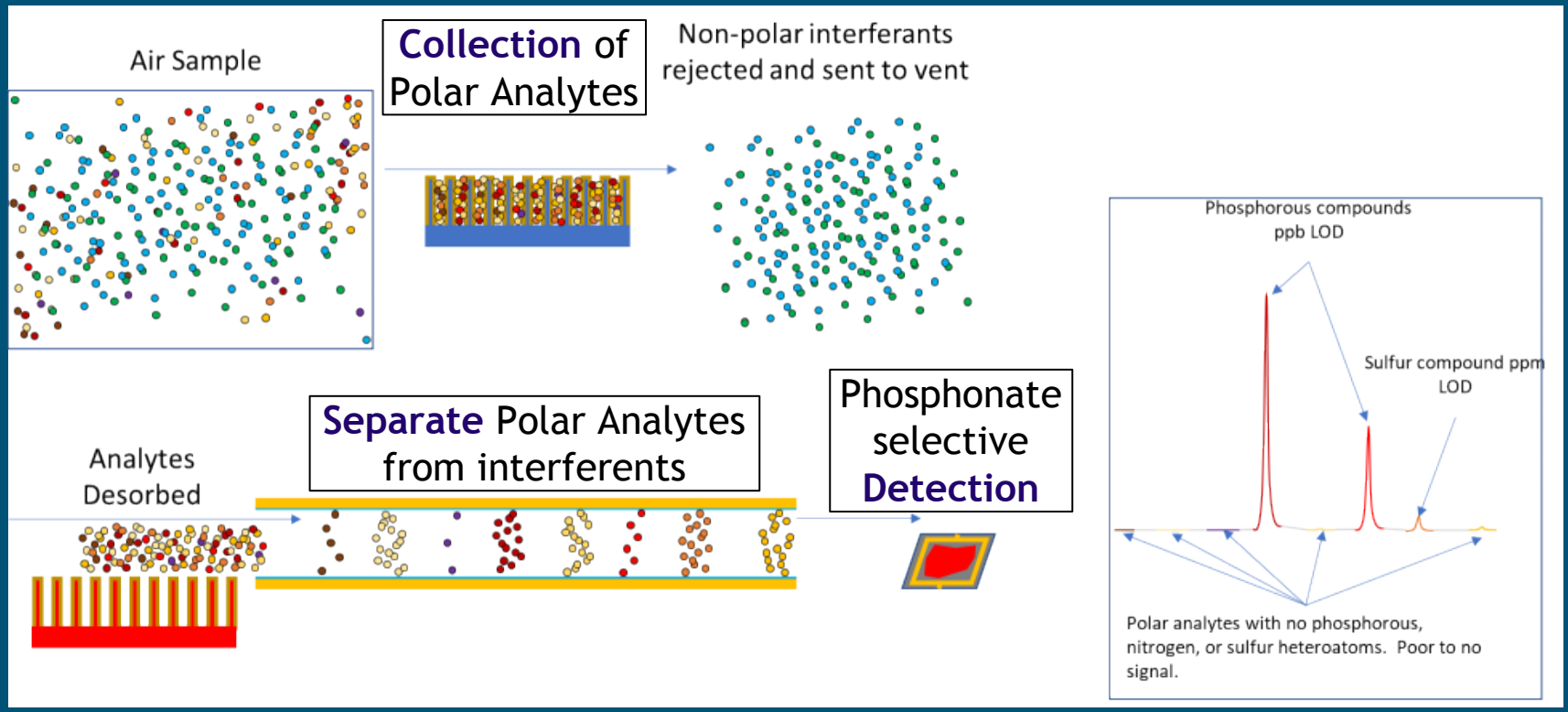
µChemLab™ - Using MEMS to Reduce SWaP and FAR

Over 20 years ago, a Sandia research team sought to use a core competency – silicon microfabrication (MEMS) to develop a low SWaP, low FAR system for CBRNE sensing based on evolving the early work in the field of MEMS Gas Chromatography (GC) started by Steve Terry at Stanford in 1979.

- Key challenges to overcome
  - Commercial GC systems rely on column length or a Mass Spectrometer to achieve selectivity
  - False Alarm Rates for GC based systems are directly related to system selectivity.
  - Mass spectrometry has a reliance on high vacuum to enable the charge amplification detectors to achieve the sensitivity
    - Requires an alternative path to high selectivity and sensitivity

Analysis
Sandia's Solution - Distributed Selectivity

Chemical sensing systems can be subdivided into three equally important analytical stages. Each stage increases the analysis surety by providing chemical information or rejecting interferents.

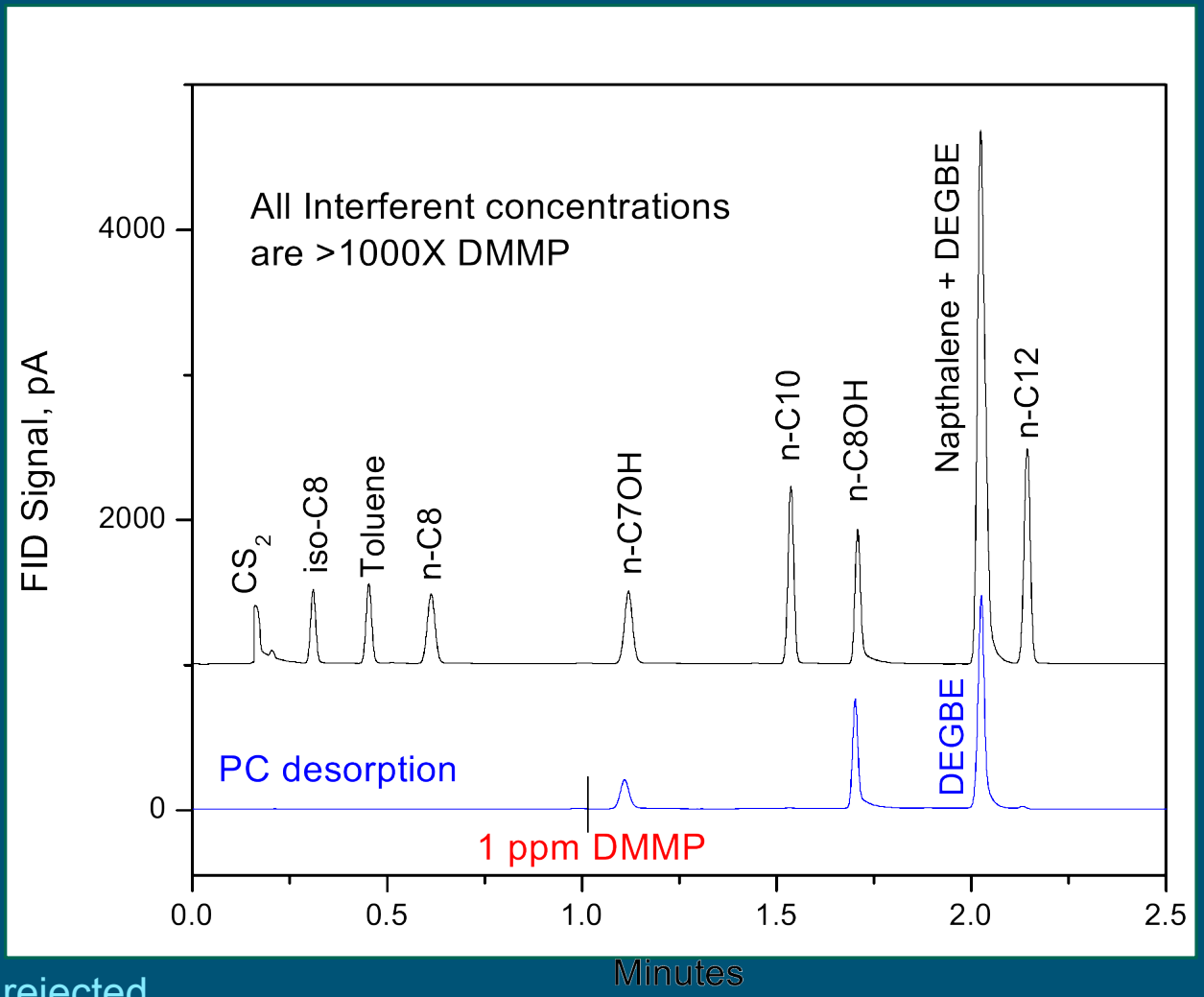


Distributing the burden of selectivity across all of the components enables lower selectivity components to be coupled for greater selectivity.

Historically development efforts have focused on only the detector stage at the expense of the other two.

Phosphonate Selective Preconcentrator Film Performance

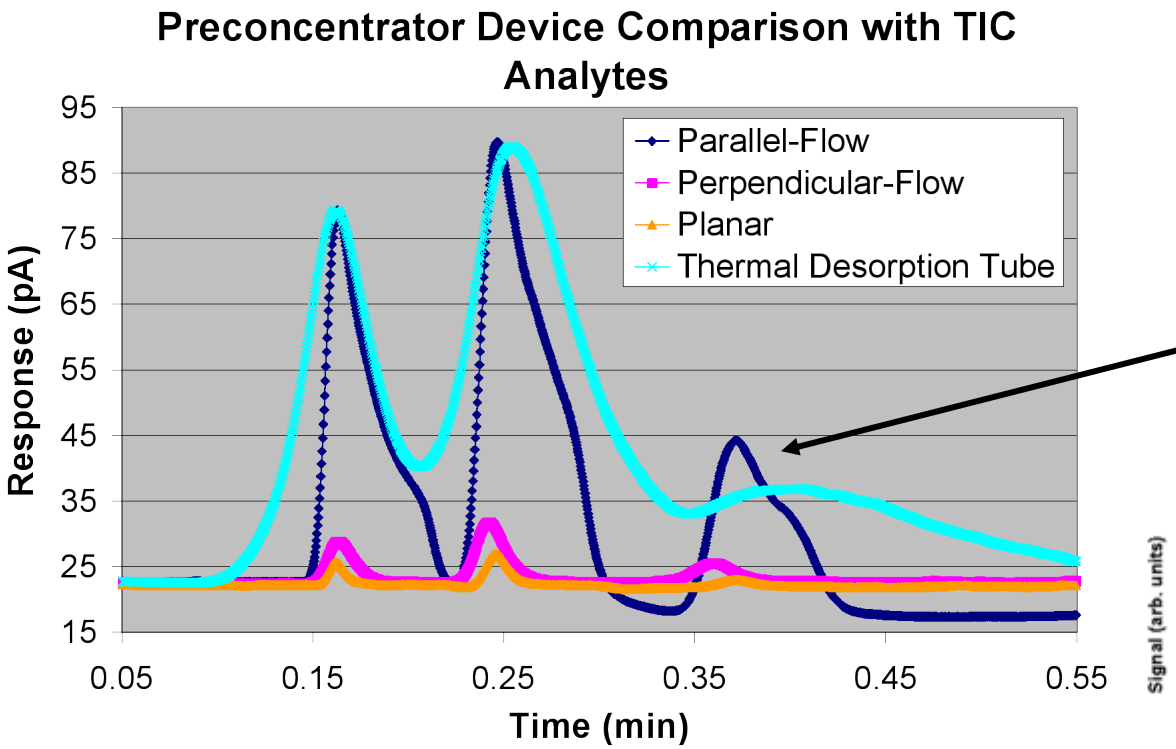
Compound	Relative Conc.
DMMP	1
Napth	6067
Water	4066 (15% RH)
Toluene	3128
Decane	1993
Octane	2002
Dodecane	2309
i-octane	1762
2-heptanol	2283
1-octanol	2177
DEG MBE	5724

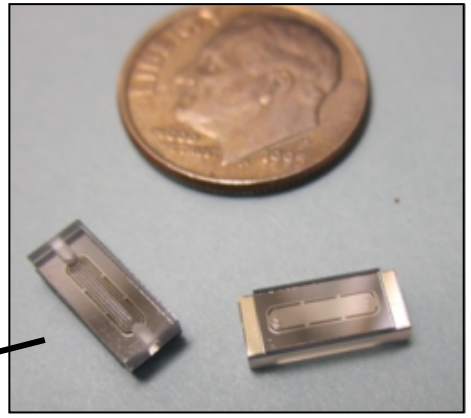


- Nonpolar interferents are rejected
- Pi-Pi polarity interferents (BTEX) are rejected
- Hydrogen bonding polarity interferents (alcohols, etc.) partially rejected.

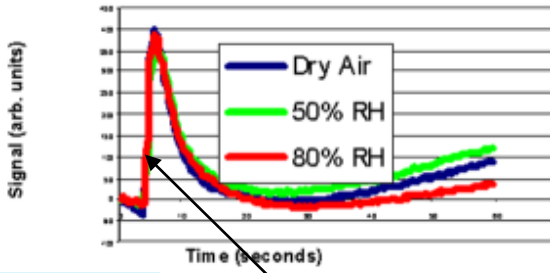
First Stage of the Analysis System

Preconcentrator design

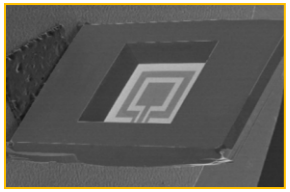




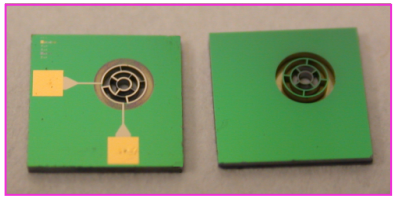
Parallel-Flow



Moisture rejected



Planar



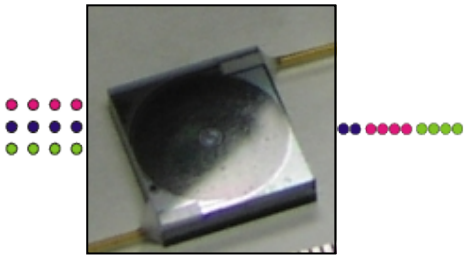
Perpendicular-Flow

Thermal Desorption Tube (commercial standard)

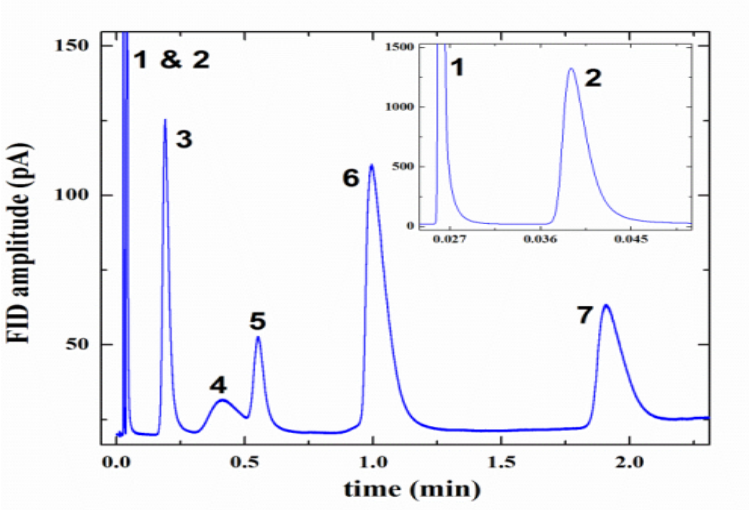
Miniature Preconcentrators compare favorably to commercial versions at better SWAP.

Second Stage of the Analysis System
Separation

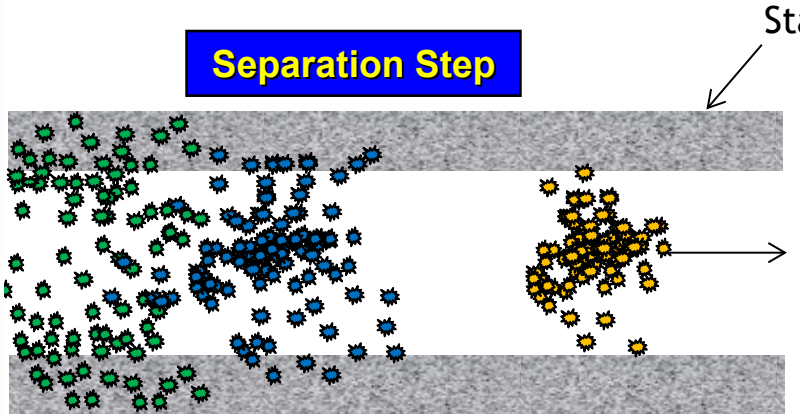
Example Chromatogram



Gas Chromatography:
- **Separates chemical species passing through a channel coated with a stationary phase based upon their affinity for the stationary phase**



Separation Step

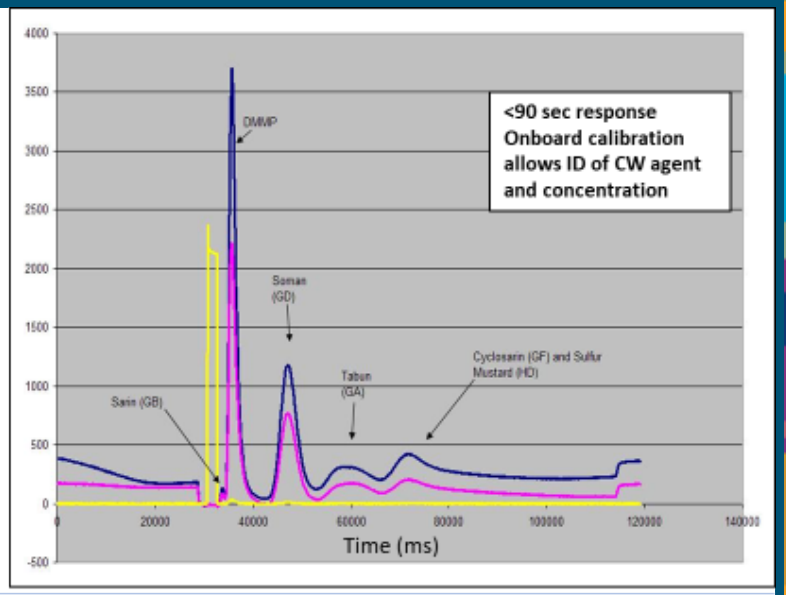


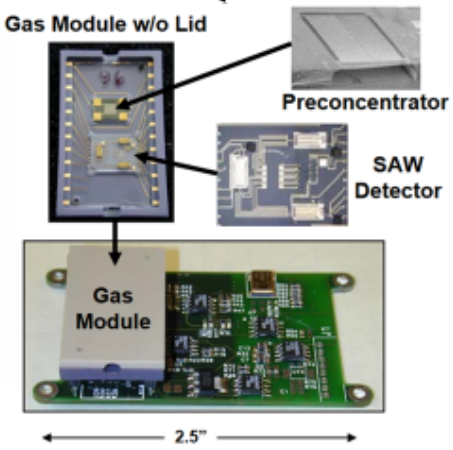
A chemical film, called a stationary phase, is deposited in a long narrow channel. The analytes passing thru the channel have differing affinities for chemical sorption into the phase. Those chemicals with greater affinity for the stationary phase (✹) are more readily retained than those with a lesser affinity for the stationary phase (✹). The time it takes analytes to transit the channel is a unique vector for identification. In this way a complex mixture can be separated into simpler mixtures or single components which simplifies the detector's task and provides additional chemical information to enable better identification. Separation is a standard methodology for the analytical laboratory.

µChemLab™
First Generation Technology Implimentations

First Generation
µChemLab™ Technology

Nearly two years of continuous, autonomous operation in subway with no false alarms and onboard calibrant



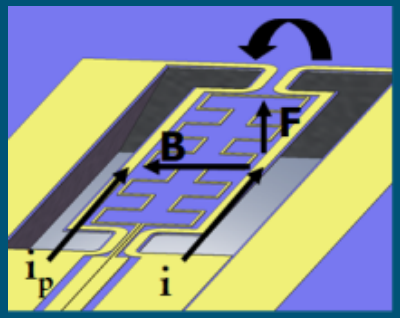


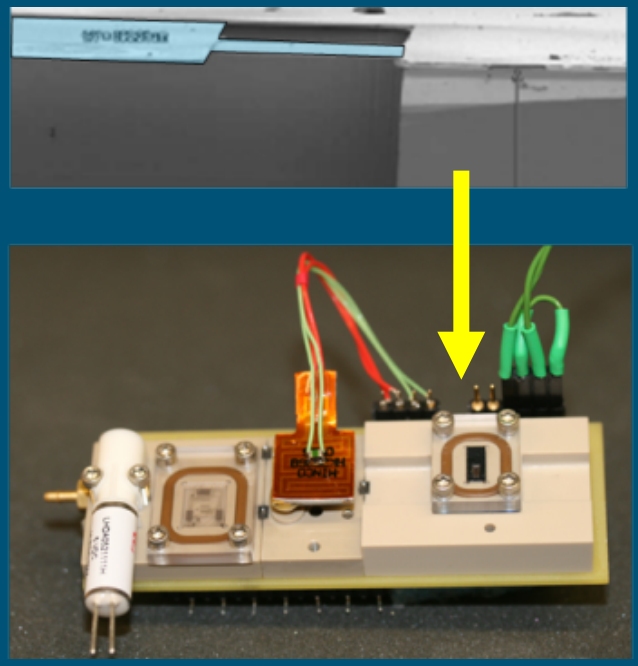
SnifferSTAR was a 2003 R&D 100 winning sensor system that mounted a µChemLab™preconcentrator and detector in a UAV wing for real time monitoring or airspace

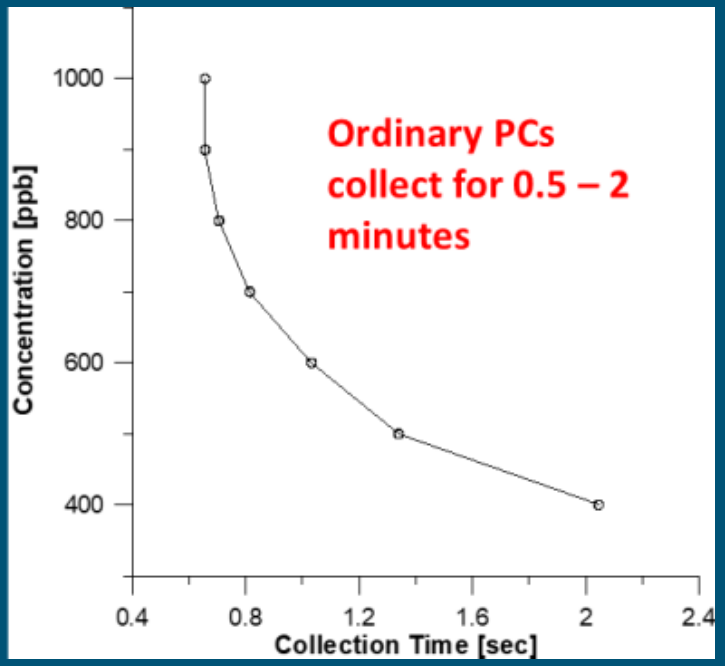
PRO-ACT: More than **450,000** analyses, Zero False Alarms

µChemLab™
Second Generation Developments

SMART PC – Pivot Plate Resonator







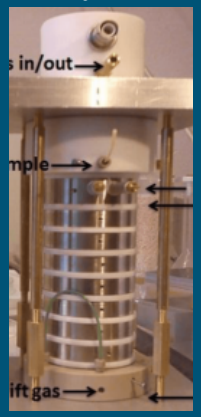
- Ultra low power and SWaP Lorentz force induced resonator coated with a sorbent film.
- Enables realtime monitoring of mass of analyte collected and dynamic sampling times, unlike ordinary PCs which collect for defined sampling times.
  - At low concentrations analyte is only desorbed into the system after a user defined mass of analyte is collected (i.e. 10-100x detector LOD).
  - While monitoring if a large bolus is detected collection can be immediately stopped and alert issued while analysis confirms identity of analytes.

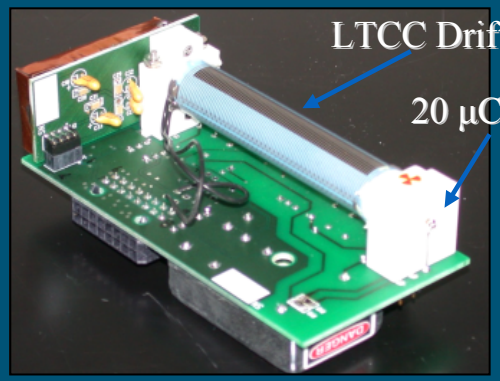
J. Microelectromechanical Systems, 17 (2008) 1396-1407; *Sensors* 2011, *11*, 6517-6532.

Detector Tradeoff Comparison
Ion Mobility Spectrometry (IMS)

Sandia's Miniature Correlation IMS (C-IMS)

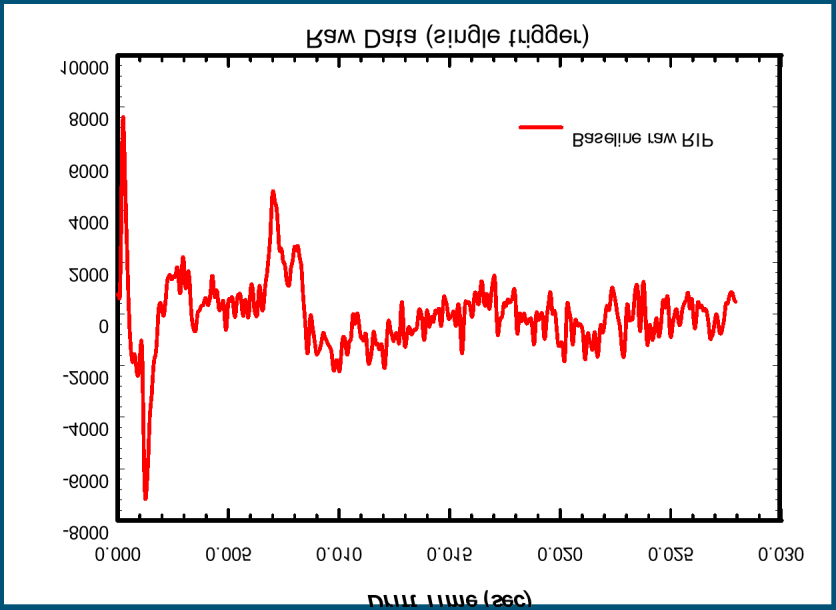
- **Operation- ionizes target compounds and measures their characteristic transit times (mobility values) through a gas volume under voltage bias.**
- **Drift time of analyte is a function of analyte charge and area**
  - **Additional Information vetor for positive identification**
- Utilizes a Low Temperature Co-fired Ceramic (LTCC) drift tube
  - Simplifies assembly
  - Lowers cost of manufacture
  - Improves reproducibility
  - Eliminates unswept dead volumes along drift tubes which cause:
    - Carryover, noise and peak broadening – poor performance
- C-IMS sensitivity comparable or better than MS
  - Sandia's correlation technique greatly improves system signal to noise allowing order of magnitude improvements in sensitivity compared to traditional IMS
- Simple, rugged construction with no moving parts
- Miniaturizes well without performance degradation
- Can operate in both a positive and negative detection mode for additional discrimination
- Uses a small Am241 radiation source (20uCi)
  - Same source as many smoke detectors enables easy transportation





6cm x 6cm x 10 cm

Single Sweep S/N



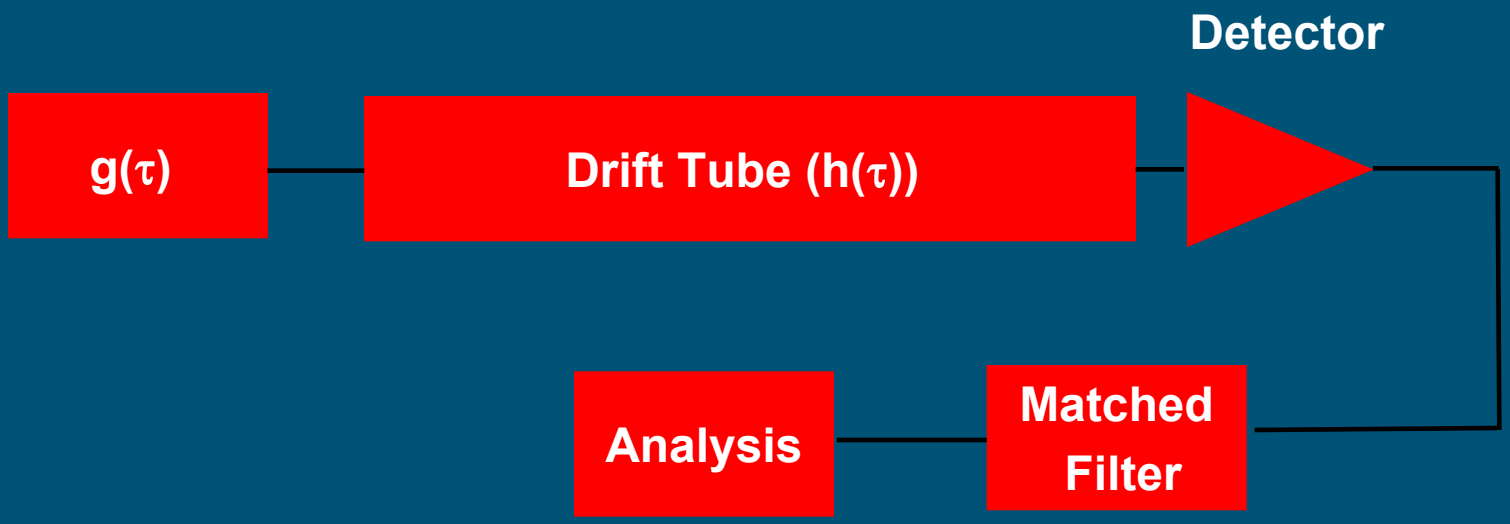
$$SNR_{ave} = \sqrt{N}\,SNR_1$$

- Detection requires chemical signature to remain constant during N sweeps.
- Achievable SNR is limited in *transient* chemical systems such as µ-Hound™.
- **Pulse Compression/ Barker Coding allows increase in signal energy while maintaining mean noise power.**

$$SNR_{peak} \le \frac{2\,SignalEnergy}{MeanNoisePower}$$

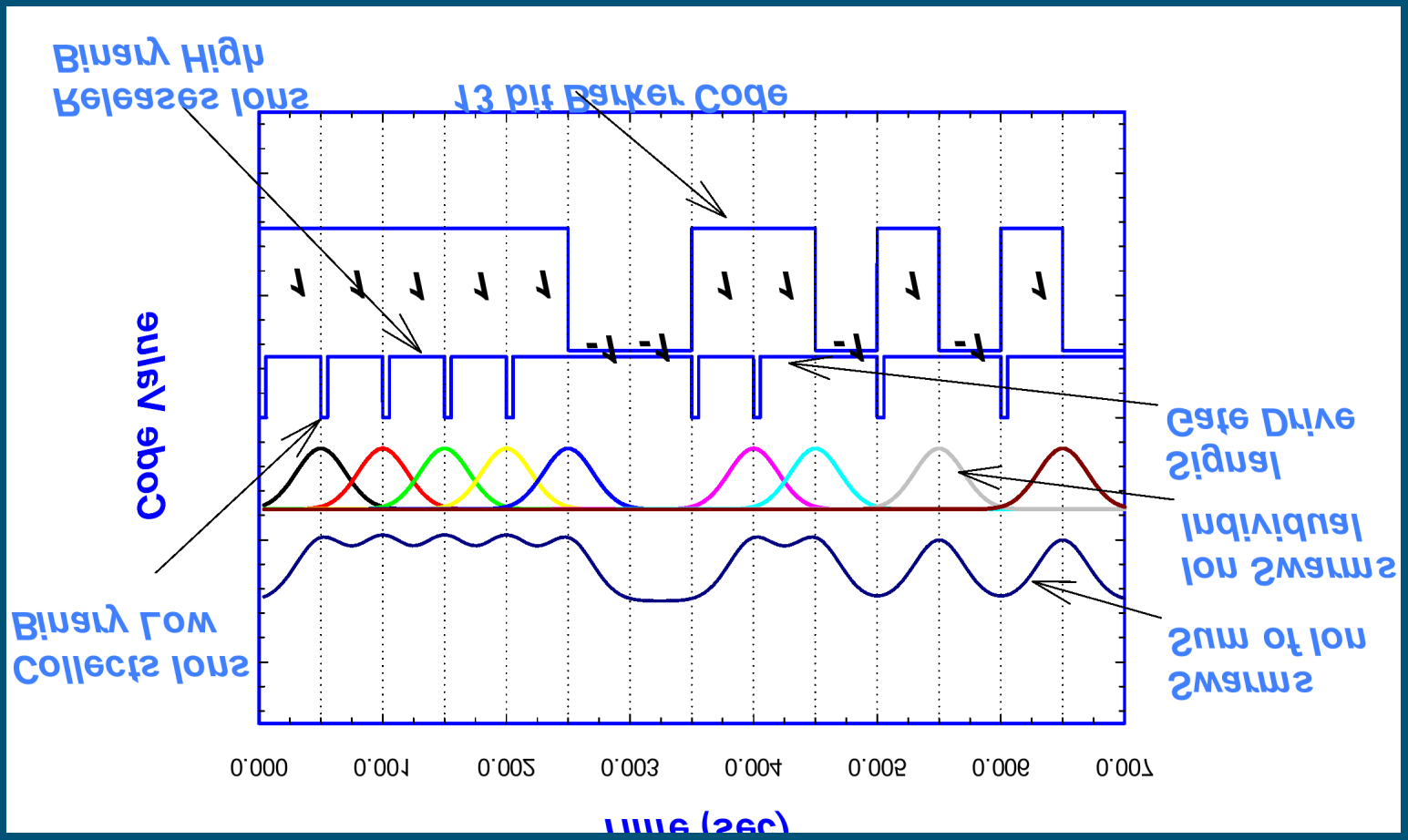
SNR is improved in *SIMILAR MEASUREMENT TIME*!!

Principle of Correlation IMS

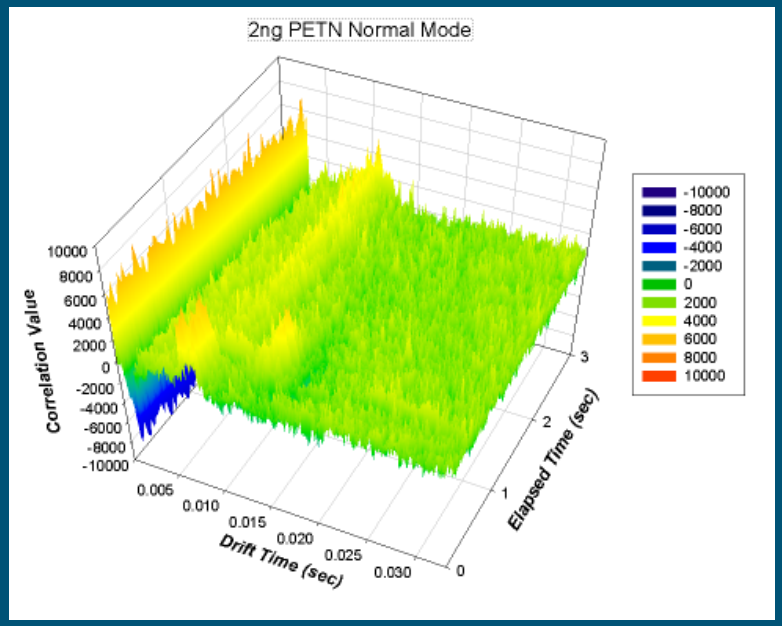


Matched filter is designed to deconvolve the convolution of the drift tube transfer function (h(τ)) with the drive function (g(τ)). *A priori* knowledge of the drive function allows construction of the matched filter. Drive function (g(τ)) can be any one of several binary or analog coding schemes including Barker-based codes or "chirped" sinusoidal drive signals.

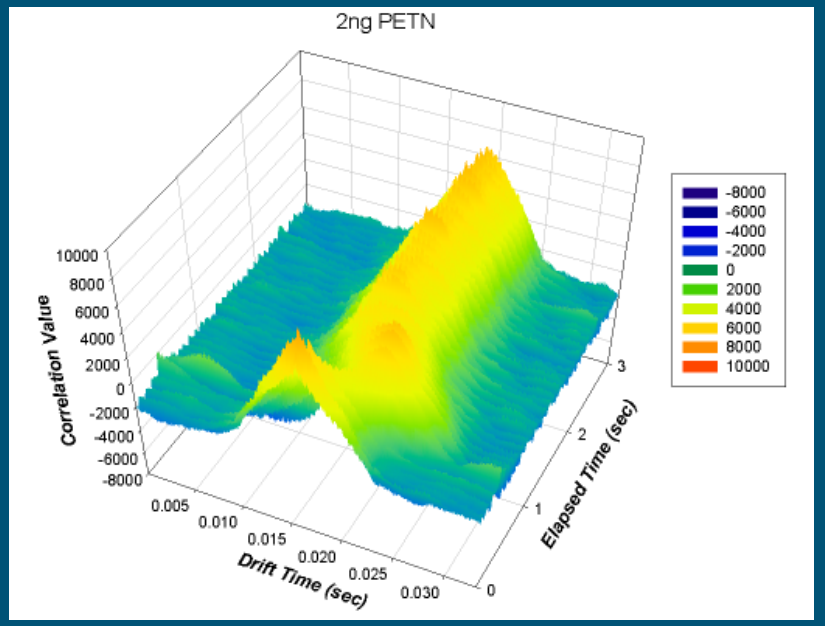
Barker Generation Approach



Signal-to-Noise Enhancement



- Single shot measurement of 2 ng PETN using conventional operation (single pulse).
- SNR_{RIP}=1.84
- σ_{peak}=1.5 msec

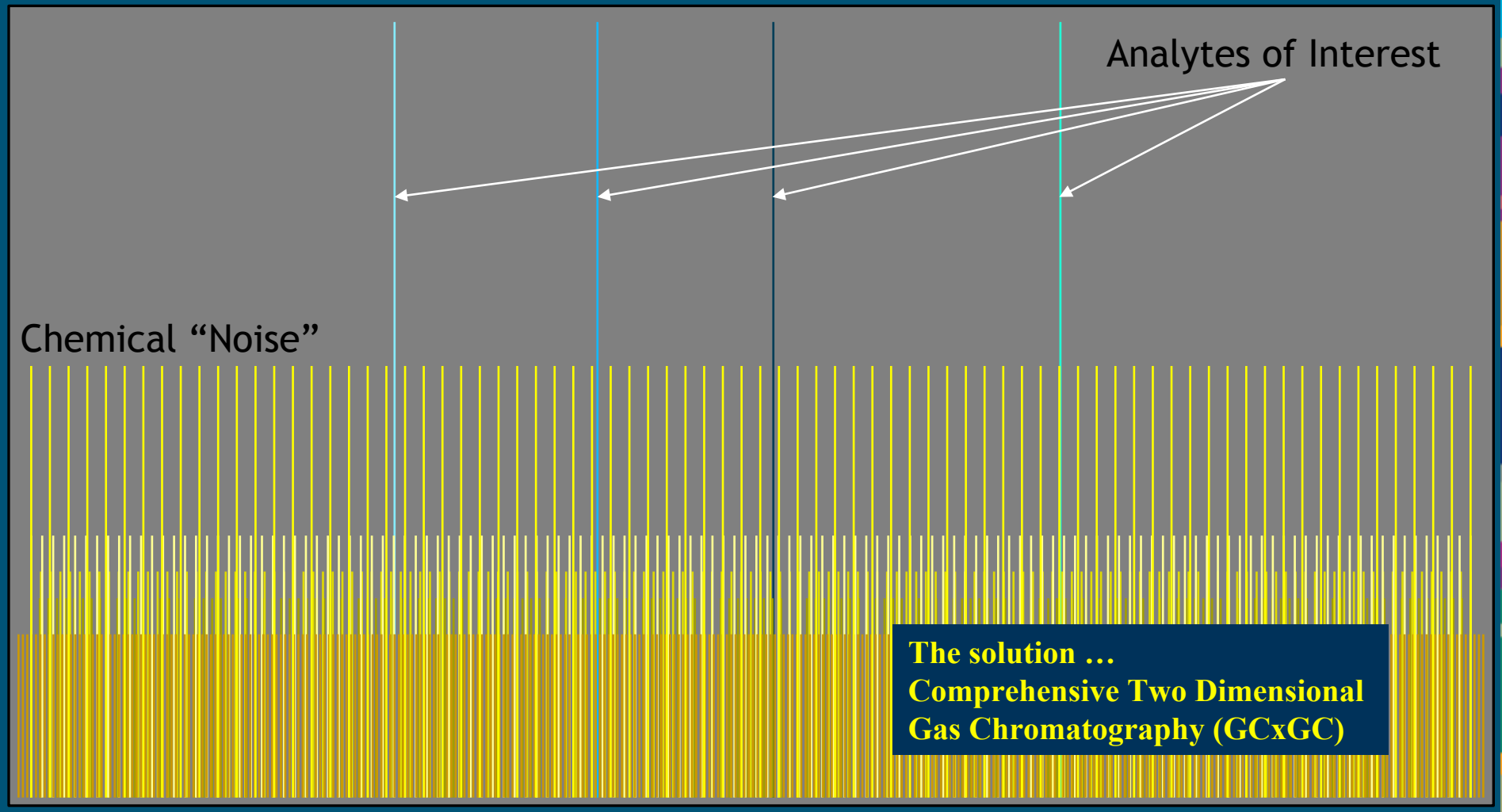


- Single shot measurement of 2 ng of PETN using correlation operation (RIP generated with pulse Barker).
- SNR_{RIP}=30
- σ_{peak}=0.13 msec

Extending the Application Range

Chemical Background
The problem… a needle in a haystack

As analyte concentrations of interest become lower the number of compounds found in the chemical background increase, increasing the chance of false alarm or misidentification



Chemical Background
GCxGC - Modulator

The heart of the GCxGC system is the modulator.

- The modulator connects two columns of differing stationary phase affinity (i.e. polar, non-polar, shape selective, etc.) in such a way that the retention time information from the first column is conserved and the added retention time information from second column introduces a new information vector for analyte identification.

- The typical commercial GCxGC modulator is a thermal modulator that uses a cryogen to super cool a short length of column and freeze analytes focused there. The length is then rapidly heated by a hot air pulse to release the analytes as a narrow injection into the second column. In this way the retention time of the first column is conserved because the frequency of this pulse is known.

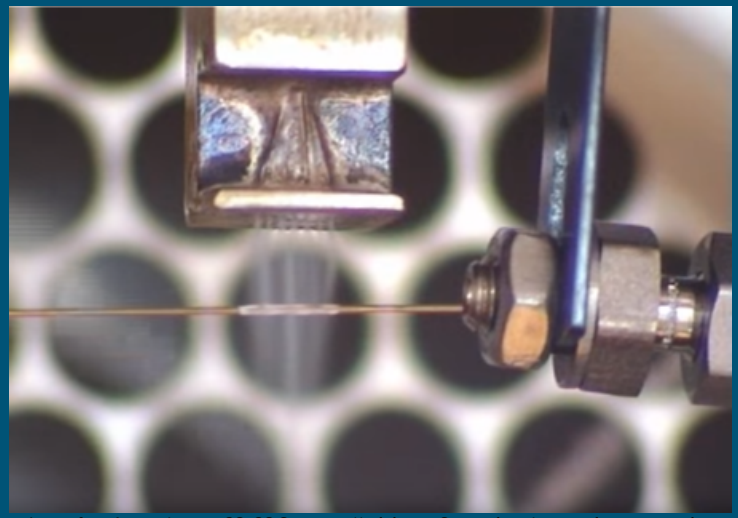


Image from **Interscience - GCxGC Cryogene Modulator, Comprehensive gas chromatography** video see https://youtu.be/Xc3vMSUPvIU for full video.

The modulator serves two purposes

1. Stop the migration of analytes from the first column onto the second column while the second column analysis is progressing.
2. Create a known injection time onto the second column.

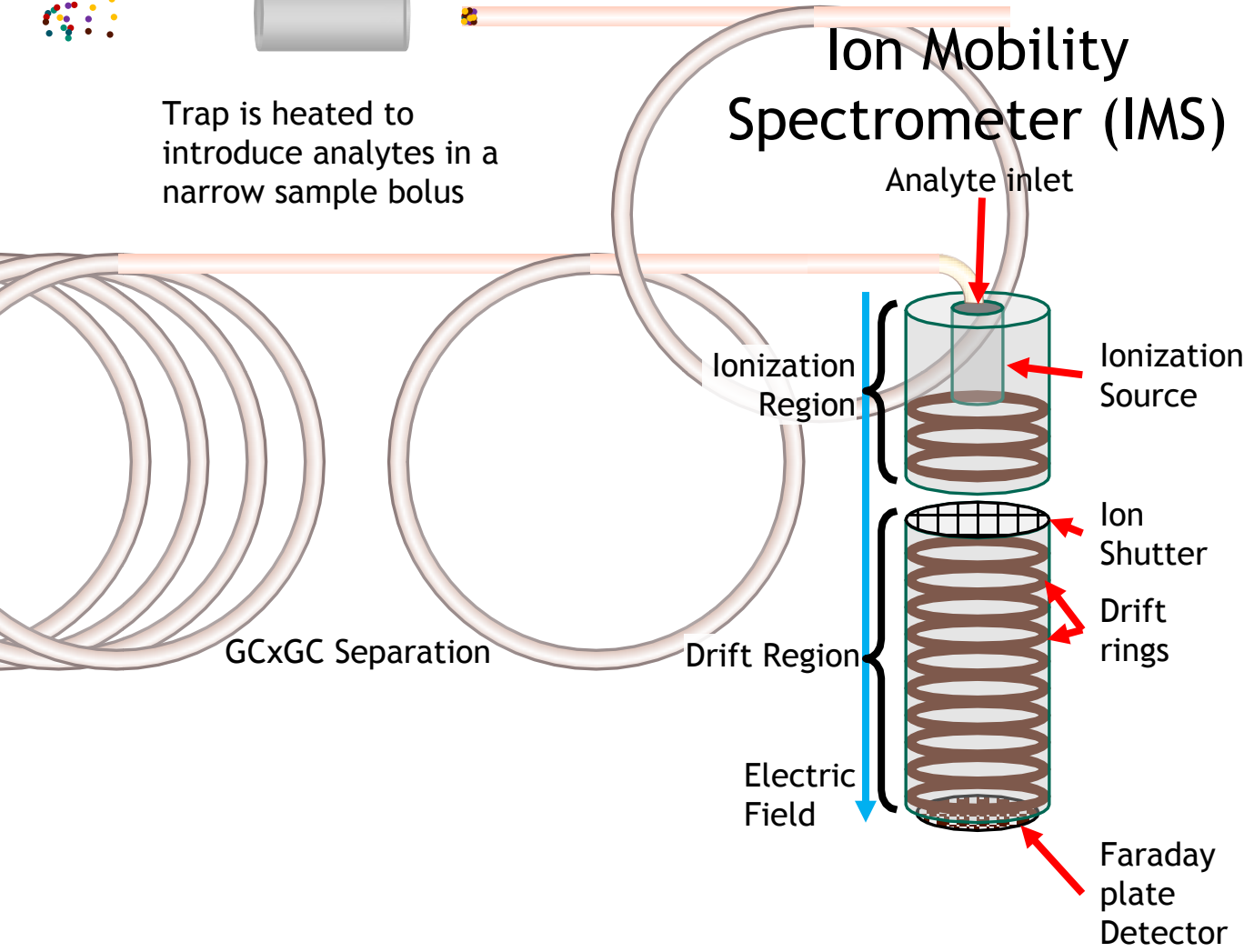
Analytes are pulled onto a preconcentrator

Carrier Gas

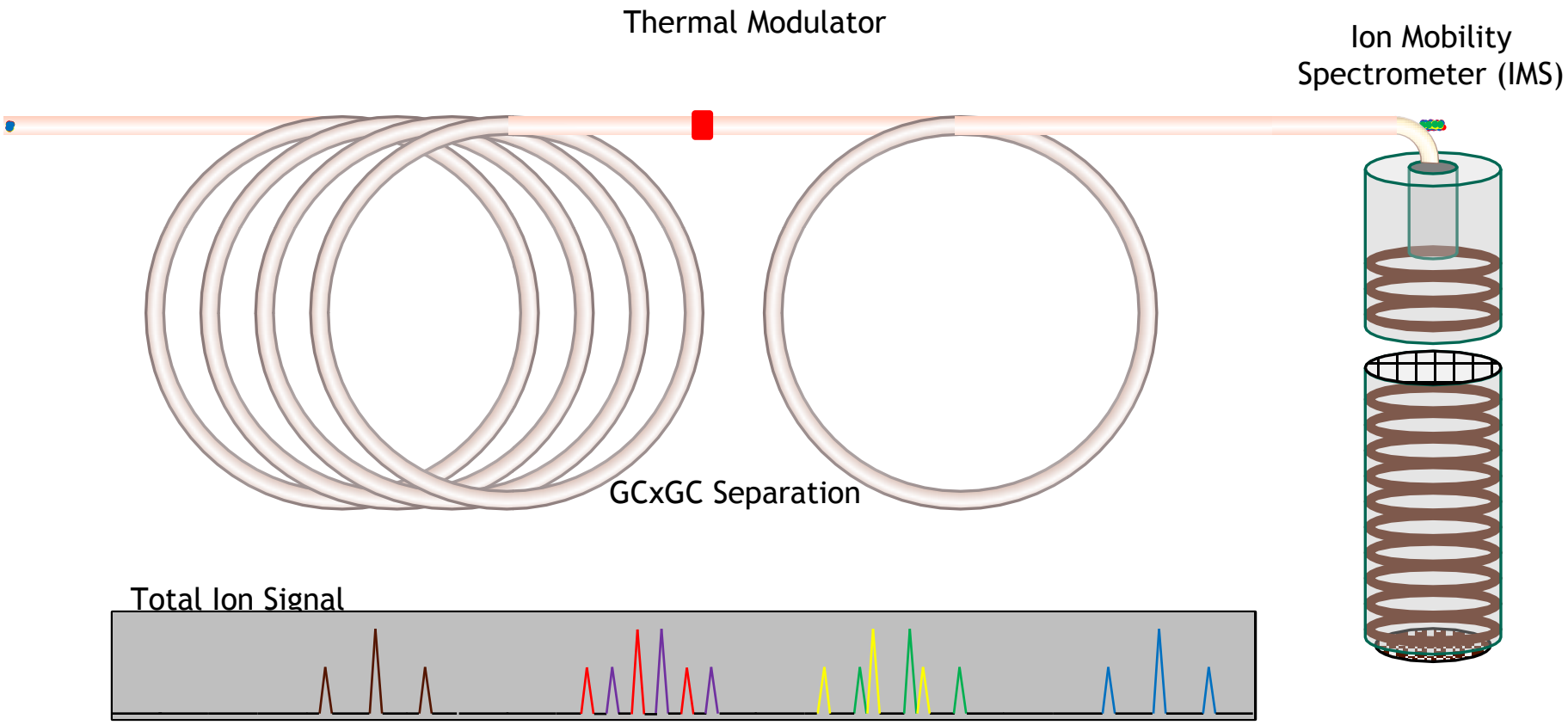
Trap is heated to introduce analytes in a narrow sample bolus

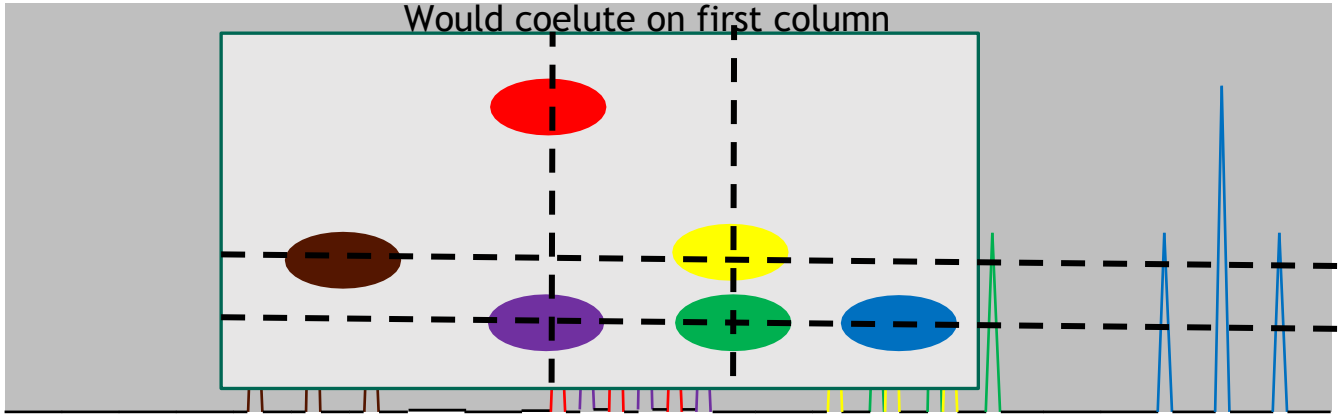
GCxGC Separation

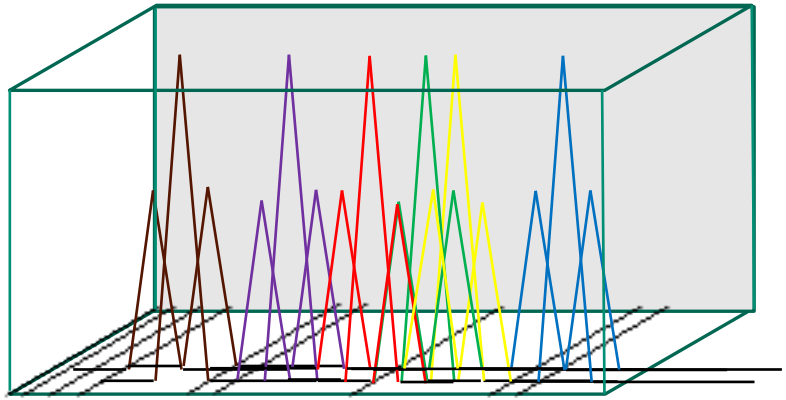
Ion Mobility Spectrometer (IMS)

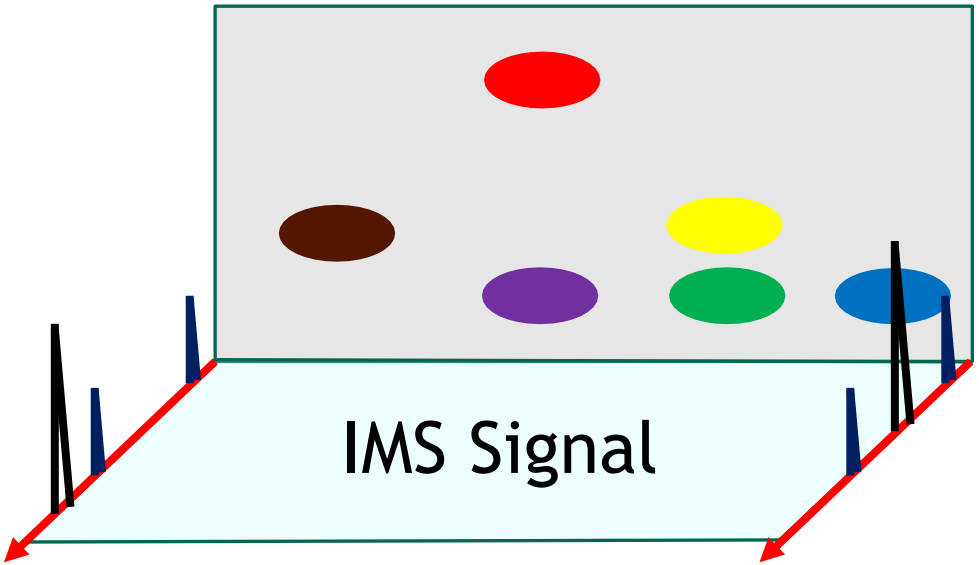


Carrier Gas


Thermal Modulator
Ion Mobility Spectrometer (IMS)
GCxGC Separation
Total Ion Signal


Would coelute on first column
Would coelute on second column





By coupling µGCxGC with CIMS adds an additional information dimension. Any analytes that happen to coelute in both GC dimensions has a third dimension to separate in the drfit tube of the IMS.

If the stationary phases are chosen appropriately then offers an orthogonal information axis.

Commercial GCxGC-TOFMS

- Linear Dynamic Range 4-6 Orders of Magnitude
- Total Volume ~1700 L
- Power ~ 2 kW
- 7200 kJ/analysis
- 3L of liquid nitrogen/hr
- 1.5 tanks of Nitrogen/day plus carrier gas consumption

Chemical Background

Stop-Flow GCxGC – for low SWaP GCxGC

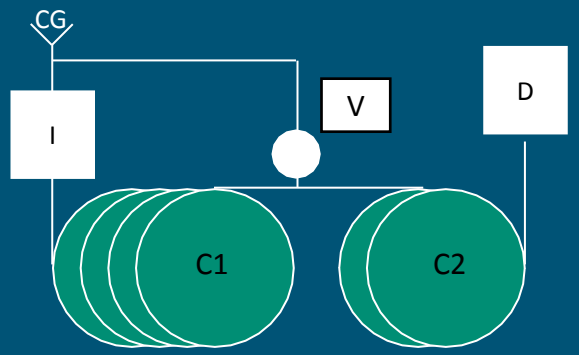
Stop flow pressure modulation

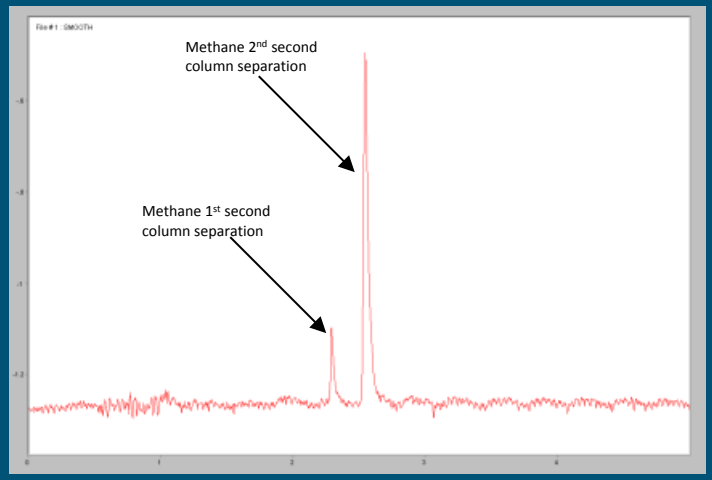
- Developed by the Sacks lab at Univ. of Michigan

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

Modified by Synovec, Gorecki, Seeley, and others for comprehensive GCxGC

- Advantages:
  - No consumables
  - Low power
  - Faster Analysis Time
  - Easily adaptable to portable instrumentation
- Disadvantages
  - Significantly less detectability enhancement unless coupled with a thermal trap as well.

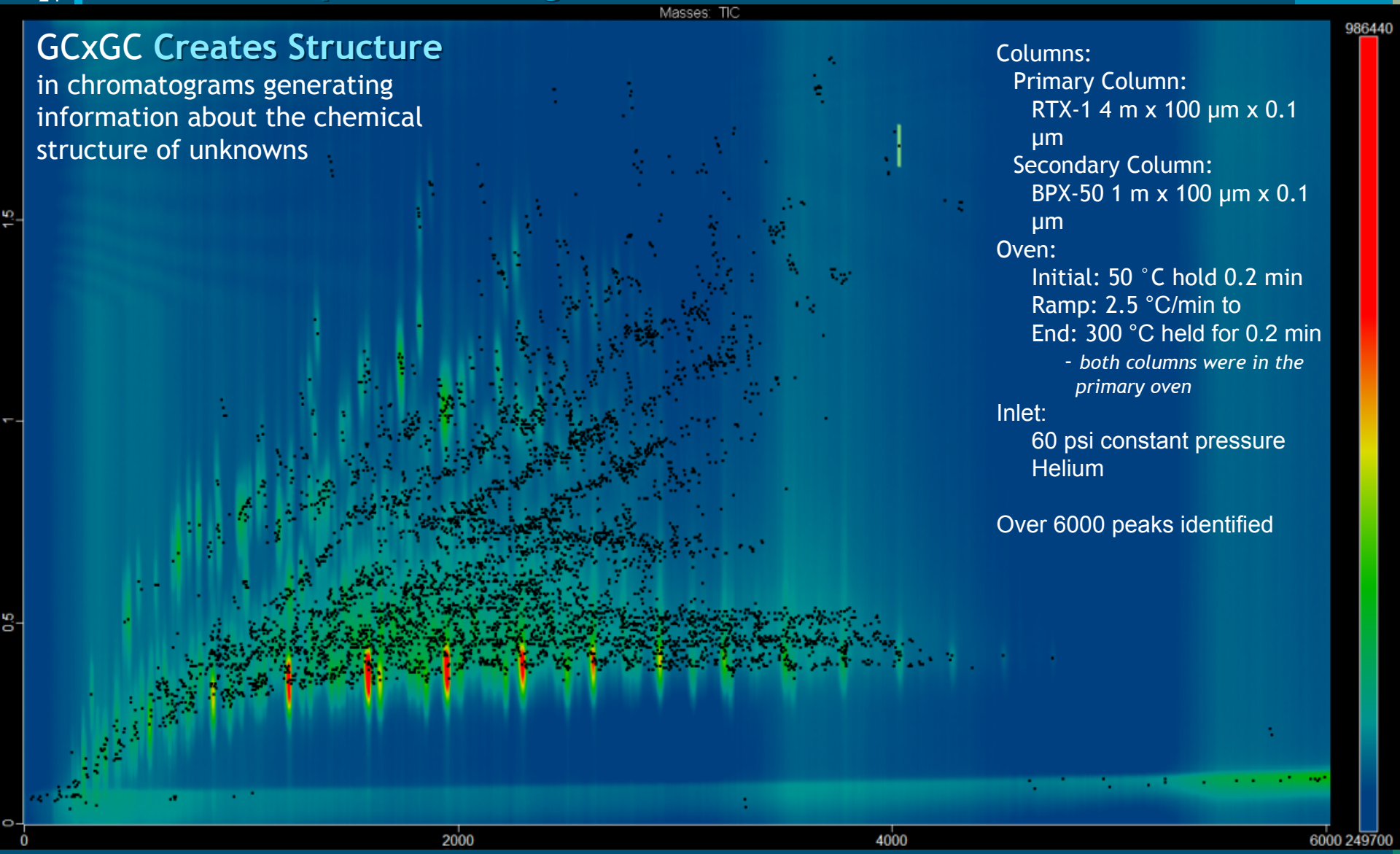




Best option for portable, low-power instrumentation currently available.

Stop Flow GCxGC

COTS Example Showing Induced Structure



GCxGC Creates Structure

in chromatograms generating information about the chemical structure of unknowns

Columns:
- Primary Column:
  - RTX-1 4 m x 100 µm x 0.1 µm
- Secondary Column:
  - BPX-50 1 m x 100 µm x 0.1 µm

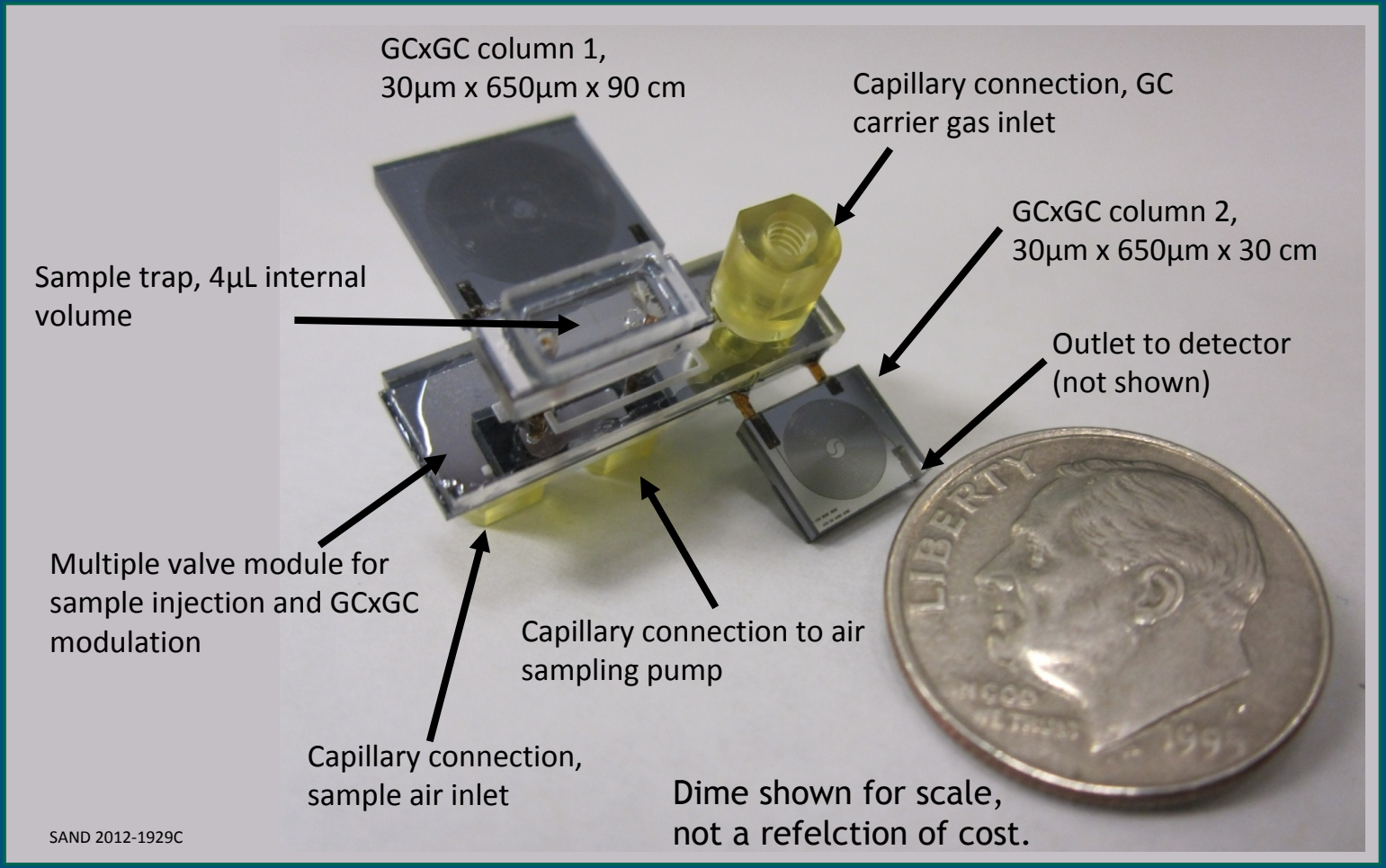
Oven:
- Initial: 50 °C hold 0.2 min
- Ramp: 2.5 °C/min to
- End: 300 °C held for 0.2 min
  - *both columns were in the primary oven*

Inlet:
- 60 psi constant pressure Helium

Over 6000 peaks identified

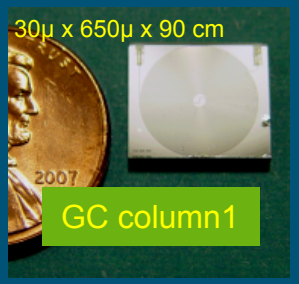
DARPA MGA GCxGC

µPC - µGCxGC with Microfabricated 37 valve manifold



Microfabricated GCxGC

µGCxGC with Microfabricated NEMS detector



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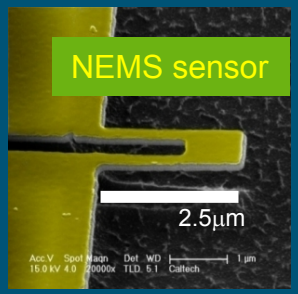
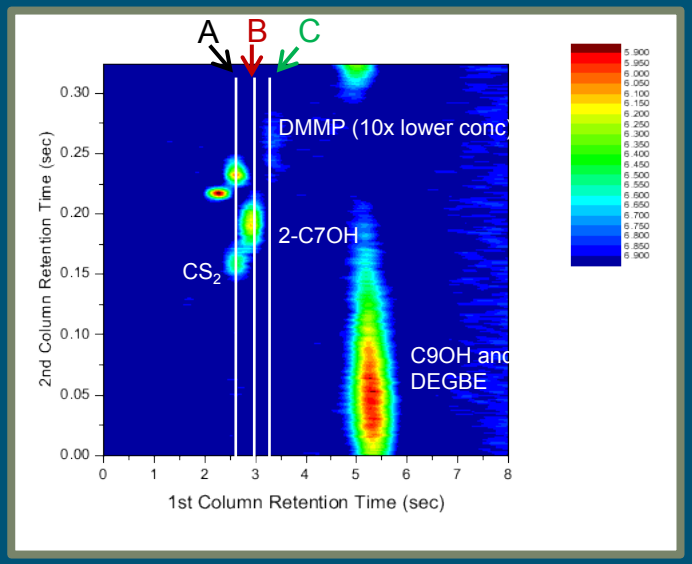
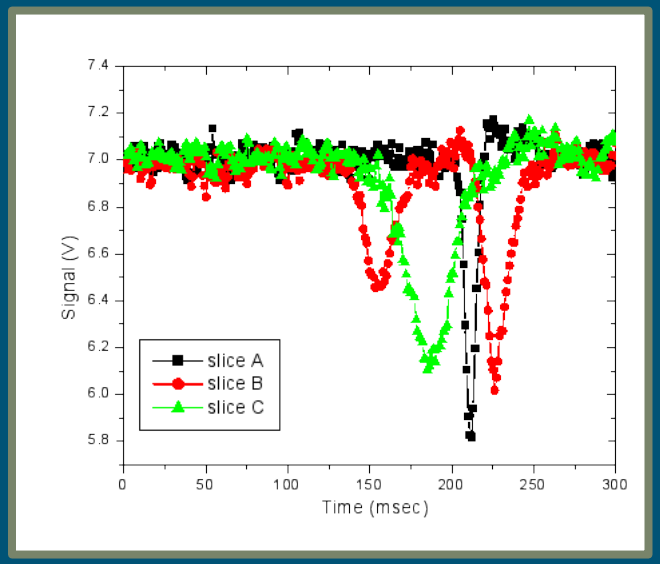






- Peak capacity shows potential of **µGCxGC** to detect **hundreds** of analytes in **seconds**

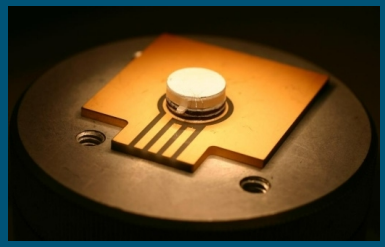
DARPA MGA Microfabricated GCxGC
False Alarm Rate Testing - µGCxGC-NEMS

- Program Goal: FAR < $1x10^{7}$
- Result:
  - No False Alarms in >20,000 measurements
  - Using statistical modeling to generate a Gausssian fit to the data at a probability of detection of DMMP = 0.95 in presence of interferants, resulted in a modeled Pfa = 1.4×10^{-12}
- Assuming a **10s** total analysis cycle this correlates to one false alarm in **~444,000 years**.
  - Caveats:
    - Assumes a limited set of known interferants with an analyte concentration 10x less than interferents concentration.
    - Real world conditions less structured and more unknown interferants are likely.
- GCxGC is the technique best suited for eliminating unknown interferants

Detector Tradeoff Comparison
Portable Mass Spectrometry

Challenges with Portable Mass Spectrometer (MS)

- **Dependent for identification on a library for comparison**
  - NIST `17: only 3/1000 in Chemical Abstract Service
  - CAS eclipses NIST every 11 days new VOCs are identified faster than NIST can be updated
- **Lack of affordable, high-performance mini pumps for MS**
  - Existing pumps are costly, heavy, and consume significant power
- **To avoid the issues with pumps, some MS systems operate using faraday cup detector which has lower sensitivity but can operate at atmospheric pressure.**

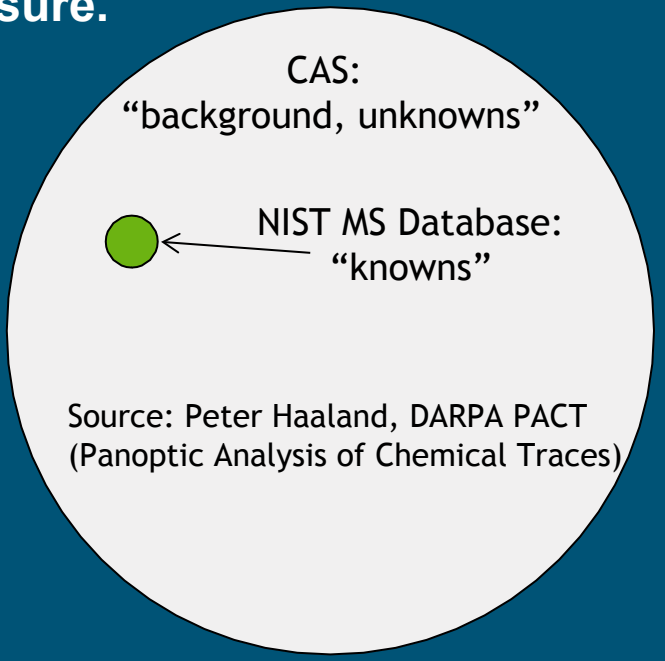


Sandia Mini MS Trap
(5 mm x 10 mm dia.)

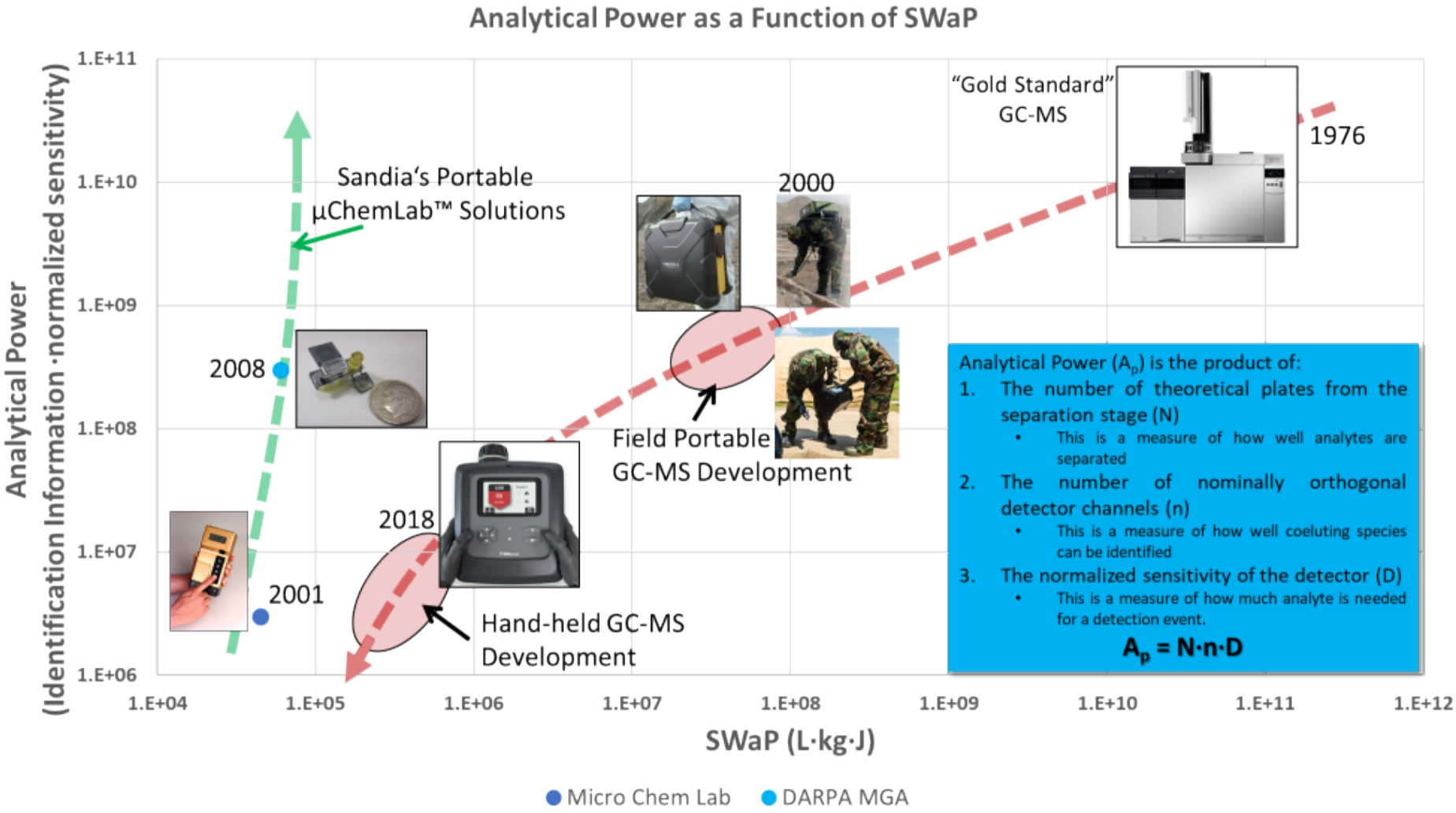
- **Long Term Challenge:**
  - High flow, high vacuum micorpumps

    Or
  - High pressure charge amplificatio

$$$
(backing pump not included)



Analytical Power as a Function of SWaP



Final Thoughts

- Fundamental physics has driven µChemLab™ design from the beginning
  - Pursuing paths that lead to enhanced performance thru size reduction:
    - Resonators become more sensitive
    - GC column resolution increases as channels become narrower
    - Preconcentrators deliver a narrower injection bolus as thermal mass decreases
- Distribution of the burden of selectivity among the analyzer stages enables better FAR performance even when individual stages perform poorer than their commercial counterparts
- Continued enhancement along this path leads to
  - Improved system performance and analytical power increases
  - Maintaining or decreasing SWaP

Questions and Contact Information

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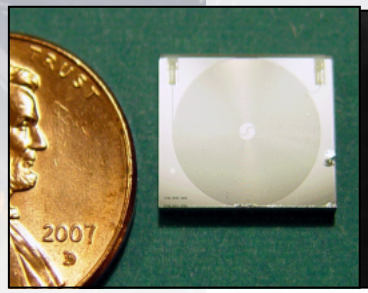
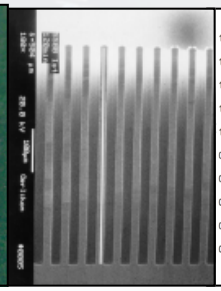
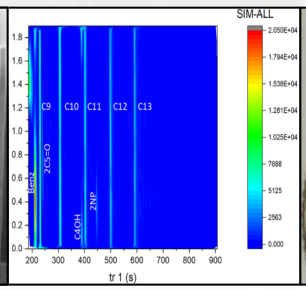
Phone: 505-845-0712

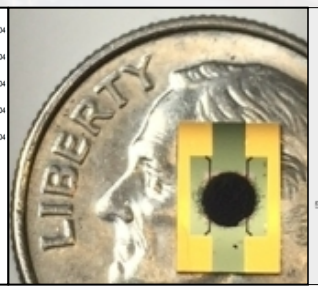
jjwhiti@sandia.gov

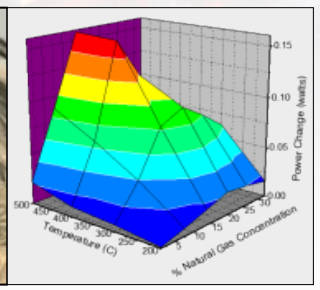
Portable Chemical Detection Systems for Chemicals and Natural Gas



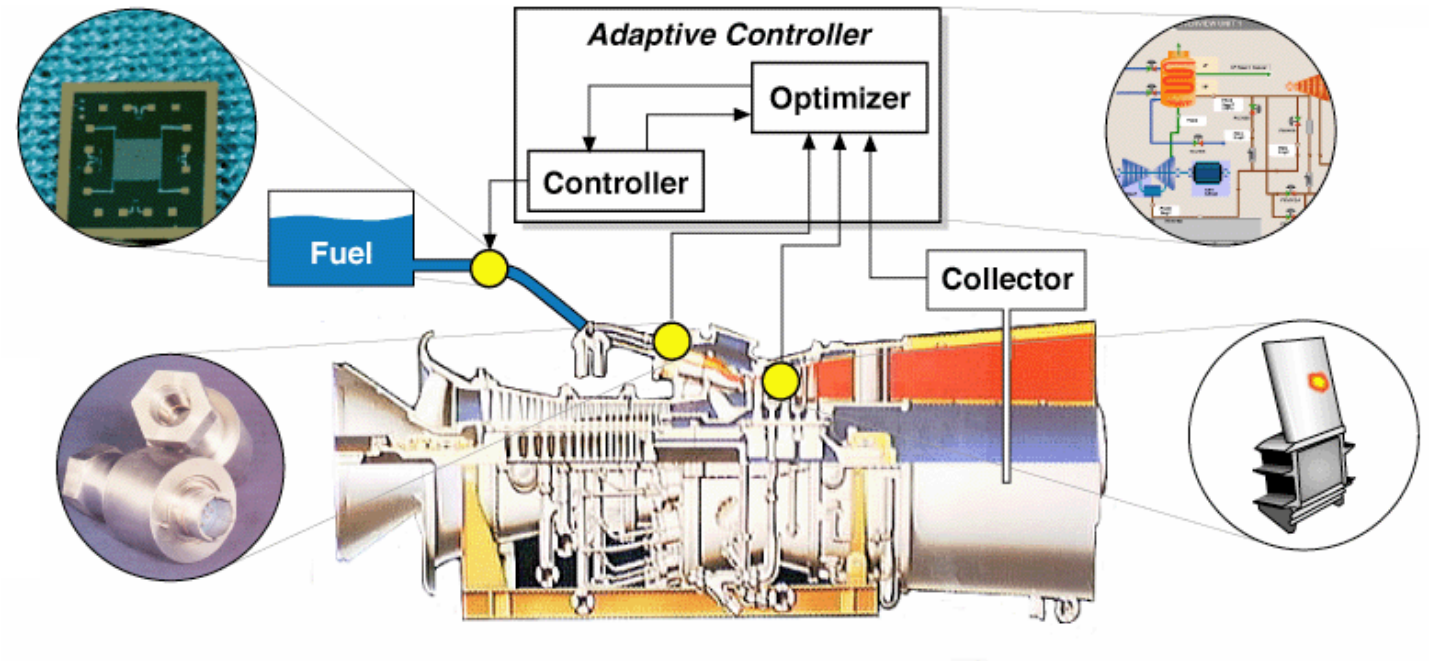








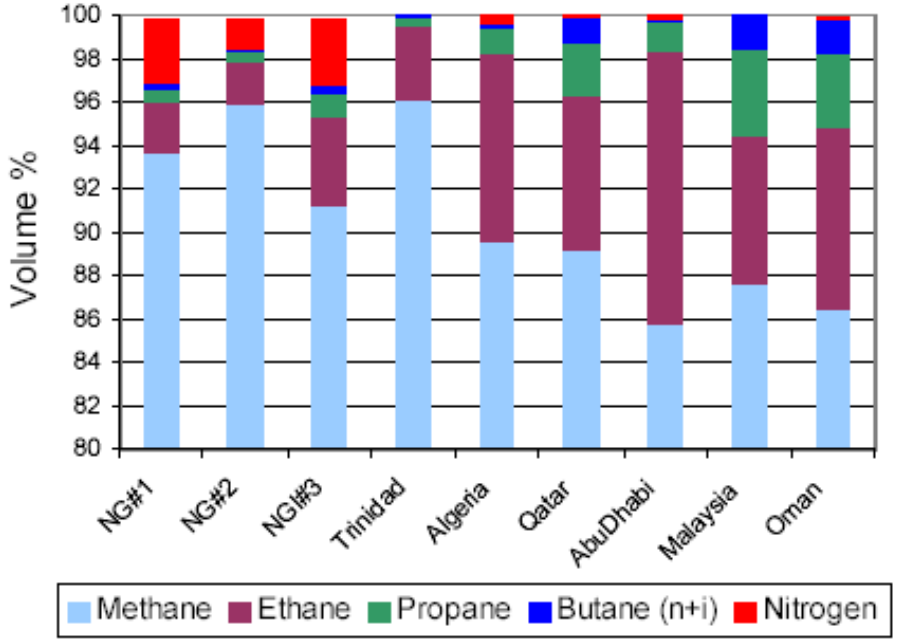
Work Motivation



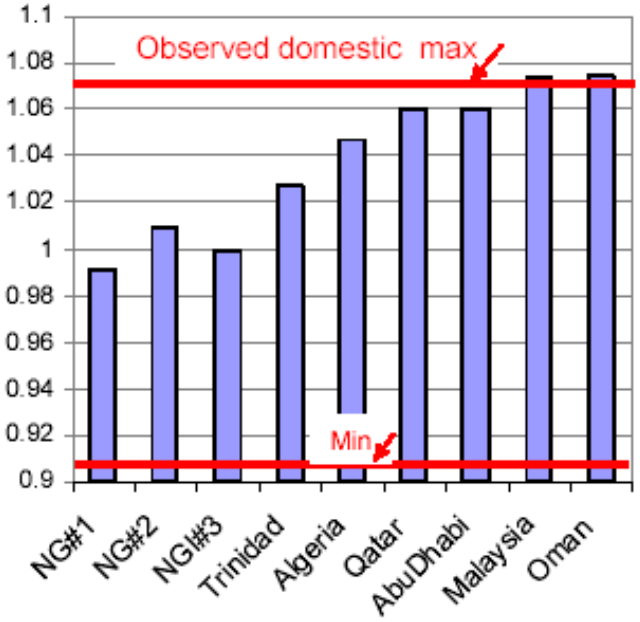
- Combustion efficiency increases can result in significant cost savings for the power generation industry.
- GC/FID/TCD analysis is not rapid enough to measure lower heating value (LHV) or Wobbe Index real time
  - To address this technical shortcoming Sandia sought to invent a faster sensor.
- Other applications include: NG monitoring, “Syngas”, Bio-derived fuels, automotive

Natural Gas Composition

- Domestic Natural Gas currently has modest variability
- International LNG supply has wider composition variability
- Projections: U.S. LNG to 6.4 tcf[1] by 2025 (22 tcf 2003 total[2]).
- Domestic unconventional gas rising to 8.6 tcf by 2025.



Derived from GRI-03/0159,Gas Interchangeability Tests:Evaluating the Range of Interchangeability of VaporizedLNG and Natural Gas, Gas Technology Institute, April 2003



Wobbe Index HHV/(s.g.)1/2 normalized by avg #1,#2,#3 gas (1336 btu/scf)

[1]. EIA Annual Energy Outlook 2005, pp. 96. [2] Ibid. pp. 95 [3] Whitepaper on Natural Gas Interchangeability, NGC+Interchangeability Work Group, Appendix A, Fig A.8

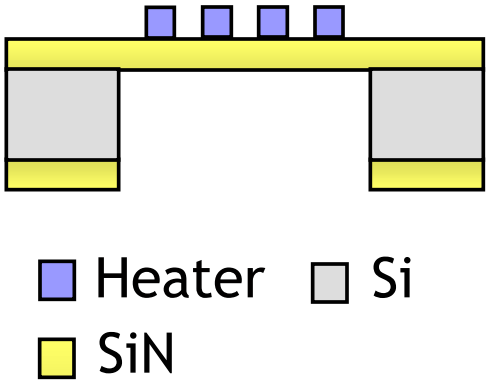
NETL

Slide courtesy of George Richards at NETL

Microhotplate Devices

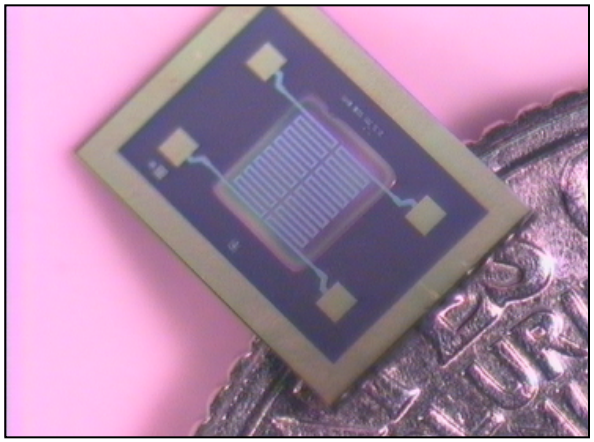
Device:

- 2.2 mm x 2.2 mm x 1 μm thick membrane of silicon nitride suspended from a silicon frame.
- Meandering tantalum/platinum wire used as a heater and a temperature sensor.
- Dielectric passivation layers over wiring.

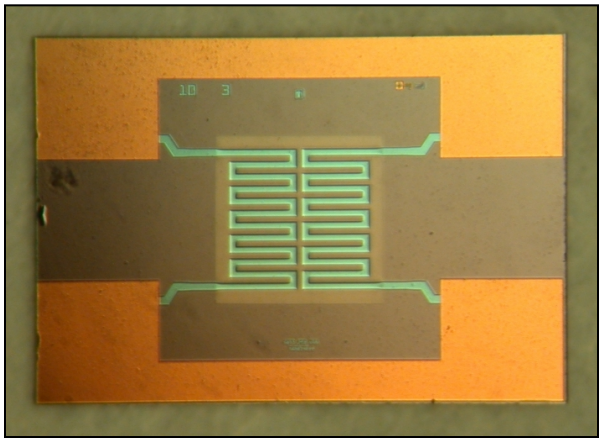


Performance:

- High thermal sensitivity, often over .4mW/°C.
- Able to attain 200 °C in less than 20 msec.



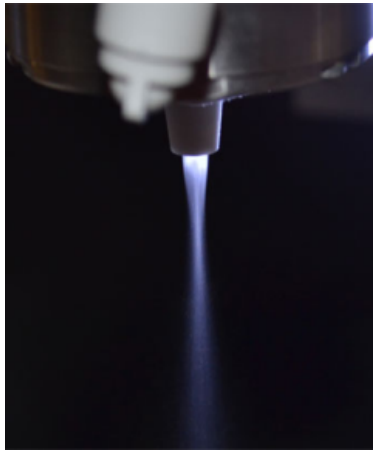
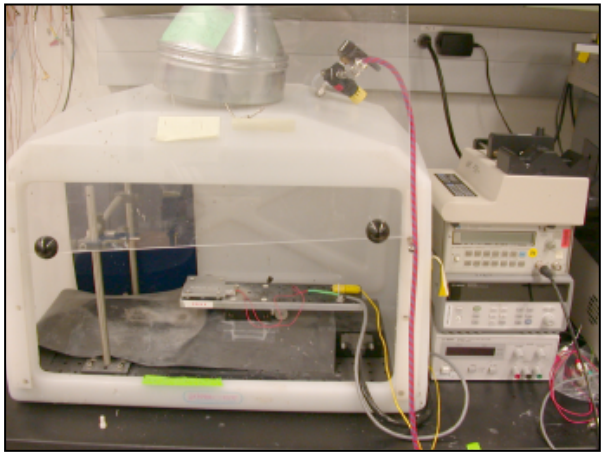
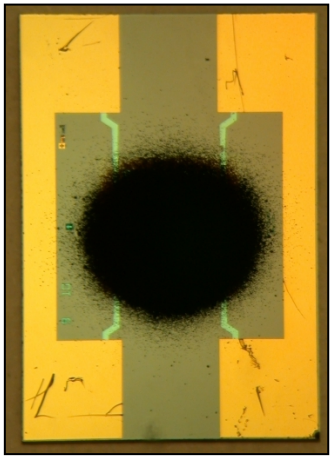
Early Microhotplate Design



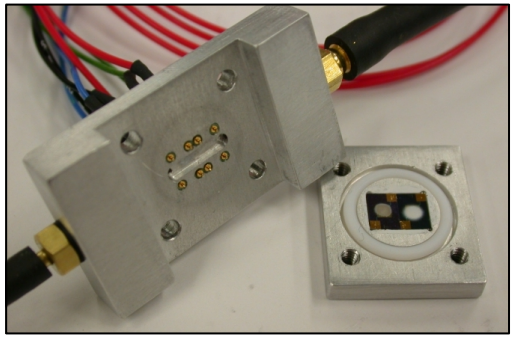
Current Calorimeter Design

Sensor Preparation and Operation

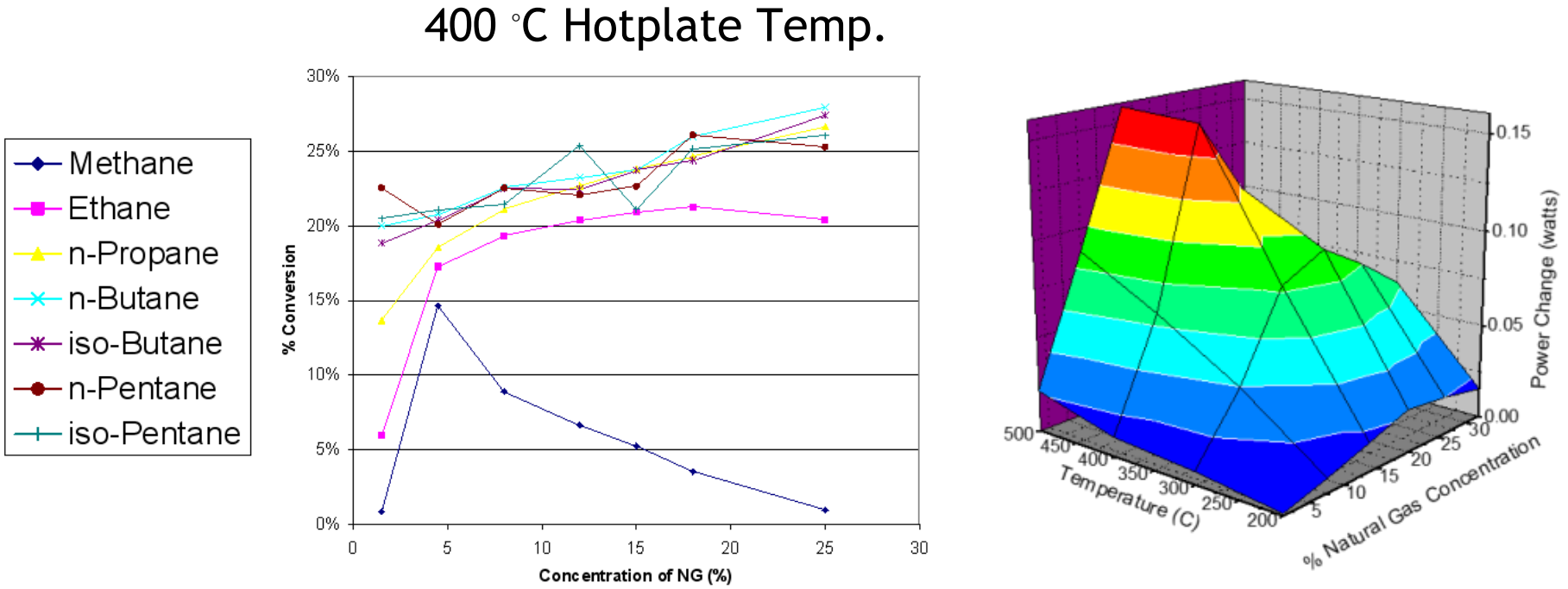
- Temperature-controlled stage aids pattern control and film definition
- Ultrasonic nebulizer with a robotic stage applies catalyst spot to microhotplate.

- Sensor fixture allows inclusion of a reference microhotplate that compensates for environmental drift.
- Temperature control circuitry monitors combustion of NG on catalyst spot.
  - This constitutes the sensor's signal.



Combustion Product Analysis



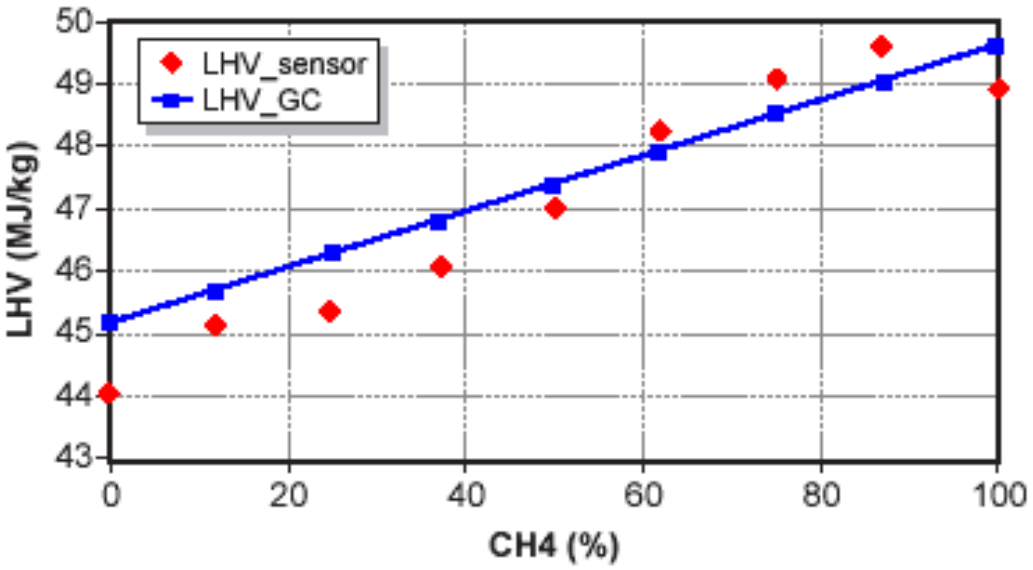
- Large differences in conversion and speciation noted as a function of flow, catalytic micro-combustor temperature, and NG composition.
- Competition for catalytic combustion sites contributes to measurement error.

Testing Results

BTU Content for Fuel Standards

Component (mole percent)	GPA Standard	Calorimetric Standard	High Ethane Standard	Helium Enriched Standard
Helium	0.50	-	-	2.00
Nitrogen	5.00	2.50	9.00	1.60
Carbon Dioxide	1.00	3.00	0.50	0.20
Methane	70.50	88.73	64.00	88.90
Ethane	9.00	3.50	12.50	3.00
Propane	6.00	1.00	7.00	1.70
Isobutane	3.00	0.40	3.00	1.00
n-Butane	3.00	0.40	3.00	1.00
Isopentane	1.00	0.15	0.50	0.30
n-Pentane	1.00	0.15	0.50	0.30
Neopentane	-	0.10	-	-
n-Hexane	-	0.05	-	-
n-Heptane	-	0.02	-	-
LHV Btu/Ft.^{3}	1180	925	1164	978

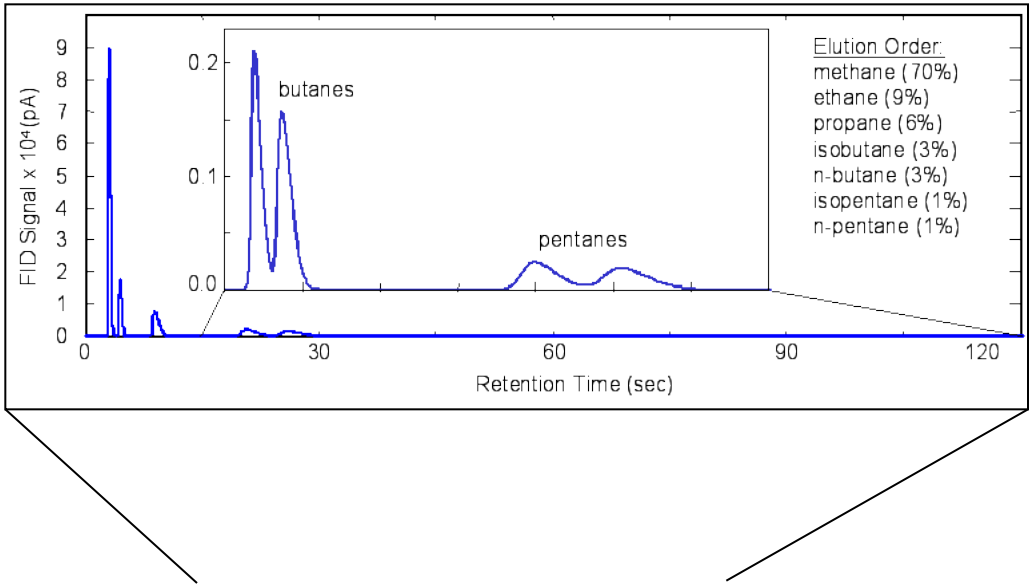
Field test sensor signal vs. reference measurement

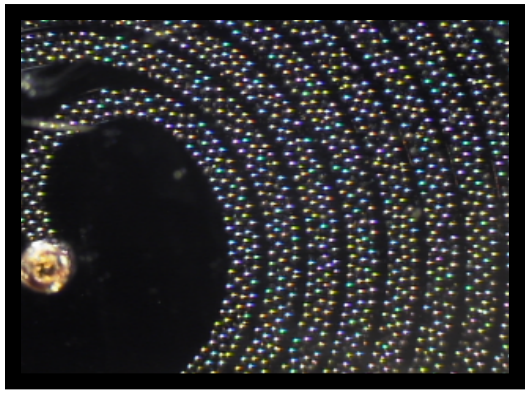


The LHV value is determined by using proprietary sensor calibration factors to associate signal with LHV content.

- Calibration determines LHV value to +/- 7% across a wide range of fuel standards and +/- 1.2% when calibrated at a field site.

Direction for Higher Accuracy Analysis

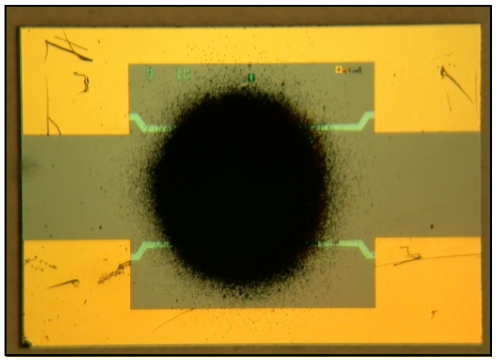




µGC Separation

Integrate Sandia's Micro Gas Chromatography technology with the catalytic micro-combustion sensor.

- Individually measure fuel constituents.
  - Reduce catalyst site competition.
- Allow calibration for each constituent's response.

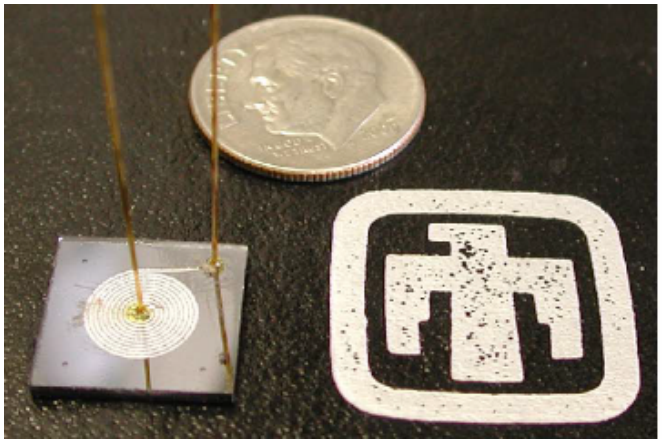


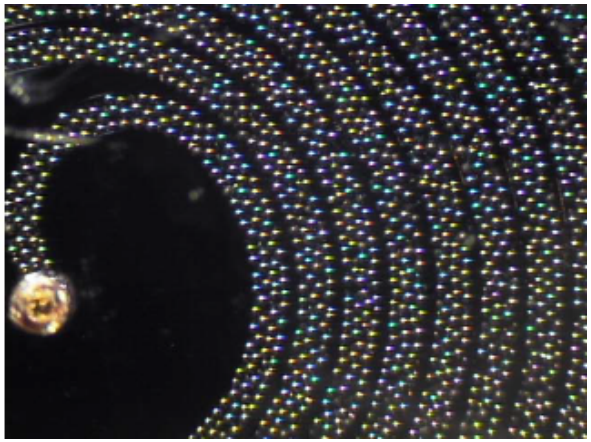
Catalytic Micro-Combustor

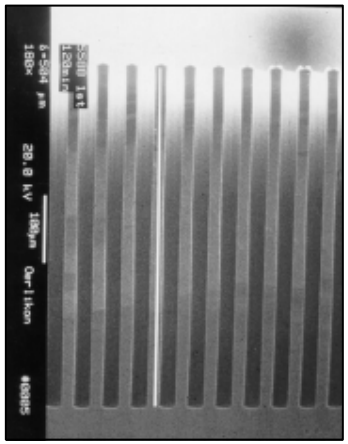
Micro Gas Chromatography (μGC) Technology

Gas Chromatography is an analytical chemistry technique that separates complex gas mixtures in time.

- Standard tool in the oil and gas industry.
- Commercial systems are relatively expensive and require skilled operators.
- Sandia has developed an alternate version of the technology using microfabrication tools and techniques.
- Low Thermal Mass of systems means no instrument sheds required
- Low power means simpler path the ATEX/NRTL certification





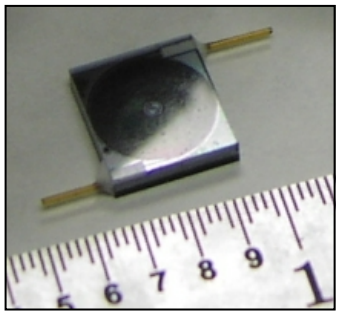


- Deep Reactive Ion Etch (DRIE) of silicon die produces high-aspect ratio, precise channel structures.
  - Can use commercial or custom packing materials.

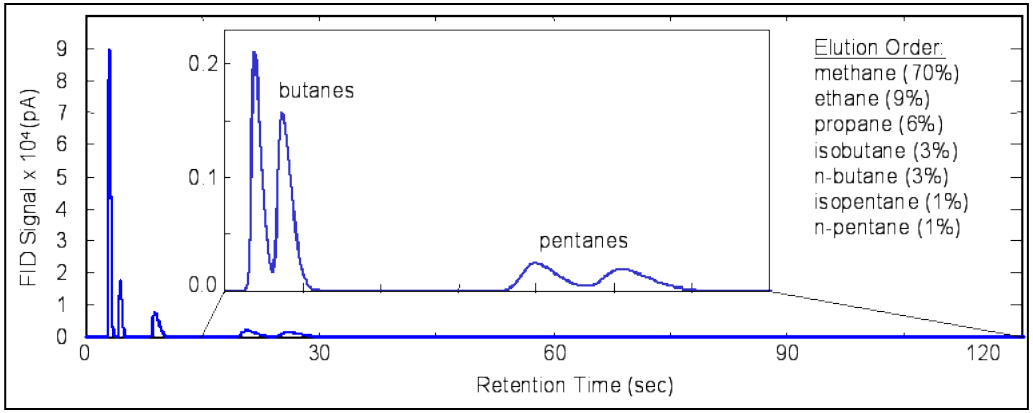
Micro Gas Chromatography (µGC) Technology

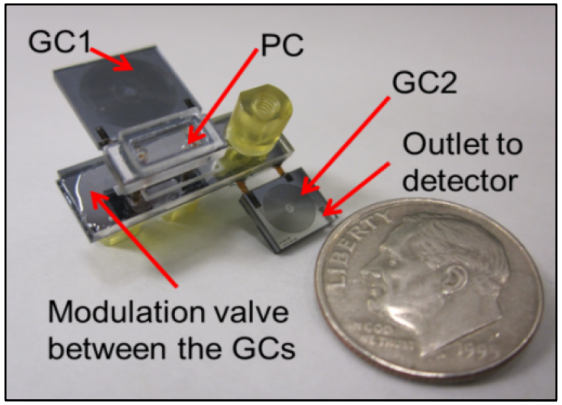
Sandia has miniaturized this technology and produced both µGC and µGC x µGC systems for analysis of complex chemical mixtures.

- Useful for NG and petrochemical analysis.

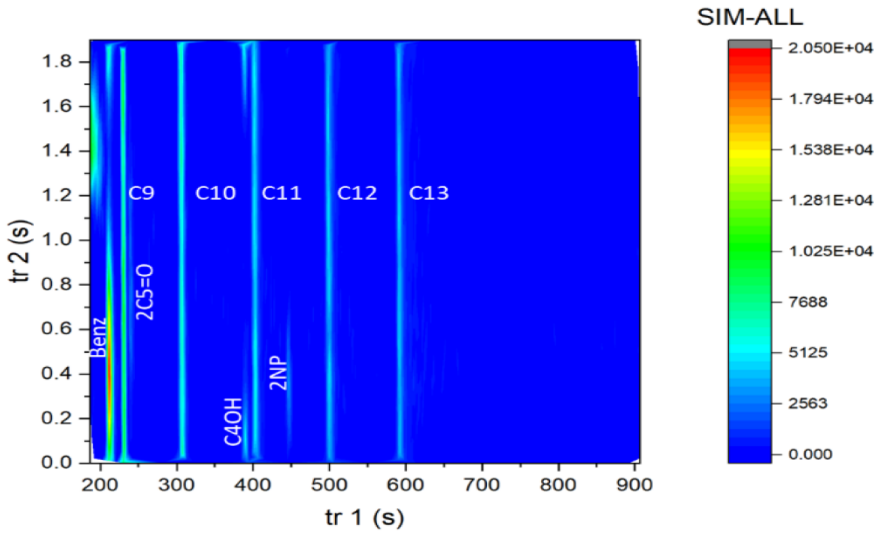


Packed µGC with commercial materials.





µGC x µGC

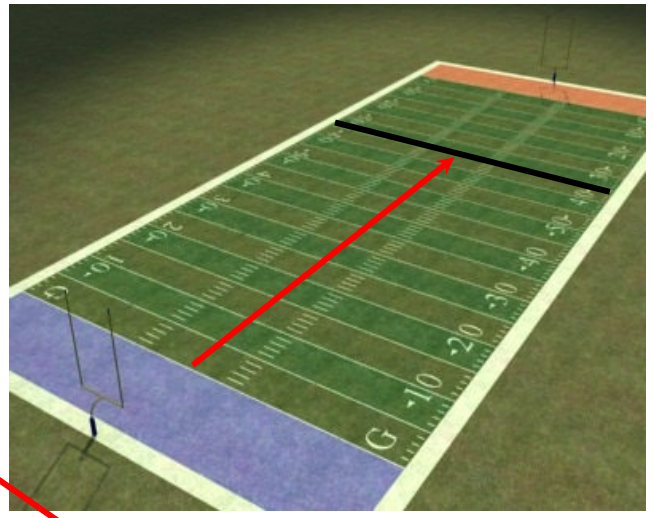


Unique µGC Materials Technology

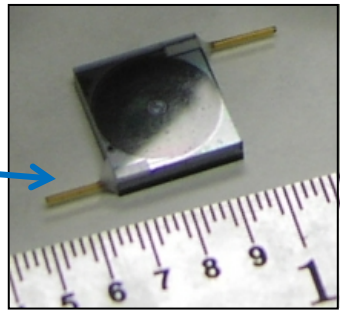
Non-polar, light hydrocarbons:
(1) Methane
(2) propane,
(3) iso-butane
(4) n-butane

Chromatogram for 60m RTX-1 GC column from Restek Archive: www.restek.com

This is for the most non-polar polymer stationary phase (PDMS) & a **65 yard-long** column.

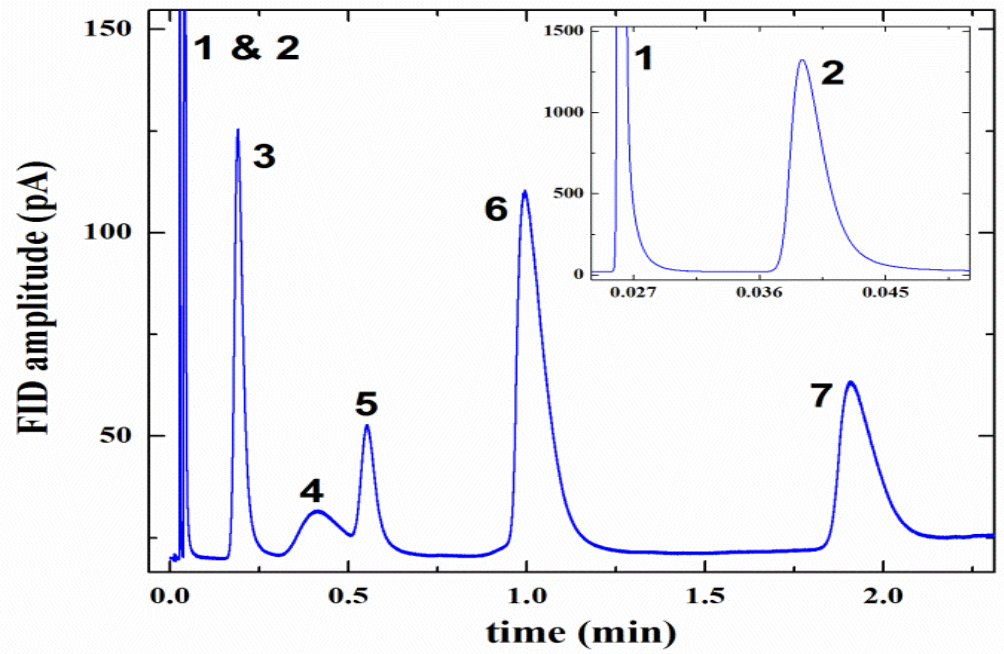


We can do this separation in this form factor.

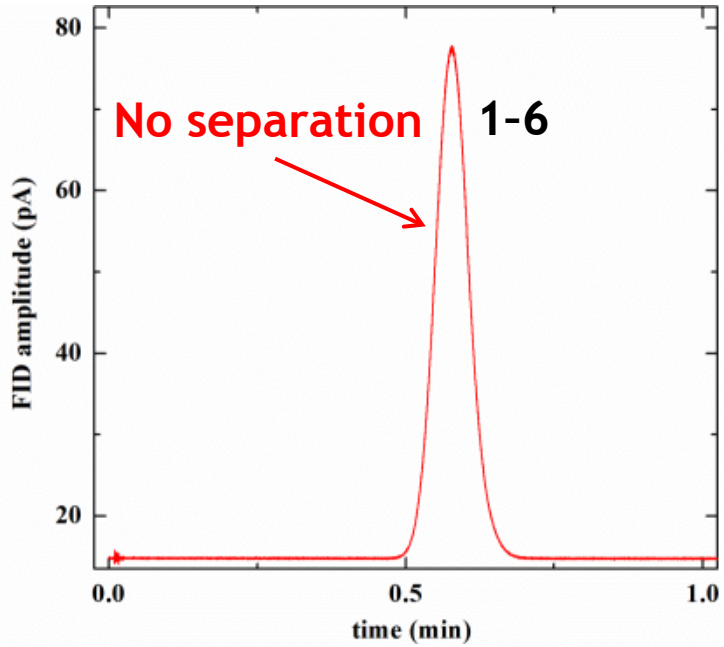


Unique µGC Materials Technology

MOF thin film, μGC natural gas separation.



μGC coated with PDMS polymer.



(1) methane, (2) ethane, (3) propane, (4) *iso*-butane, (5) *n*-butane, (6) *n*-pentane, (7) *n*-hexane

We have successfully separated natural gas components with a Metal Organic Framework (MOF) thin-film stationary phase.

- This allows higher-performance separations than a packed µGC separation (faster and with lower pumping requirements).

Field Applications

Combined µGC/Catalytic Micro-Combustor System

Early prototype combining GC and Catalytic Sensor technologies into a field-portable system.

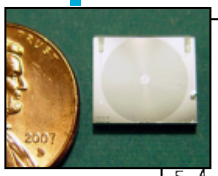
- Allow for distributed pipeline monitoring.
  - Detect fouling or leakage within the system.
- Support custody transfer applications with low cost instrumentation.

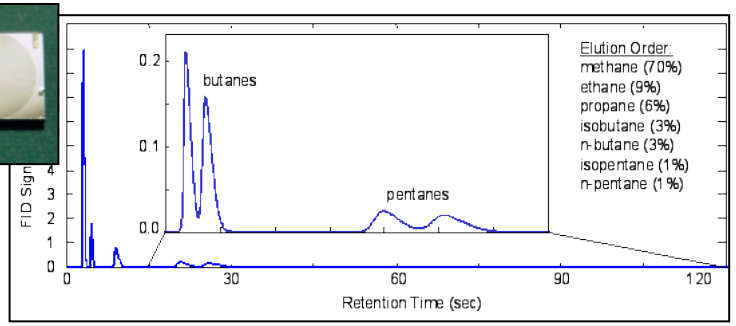
NG/Combustible Gas Detection

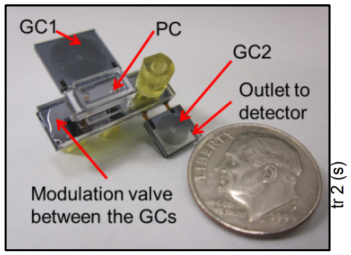
Catalytic micro-combustion sensor can detect combustible gasses and partially characterize them.

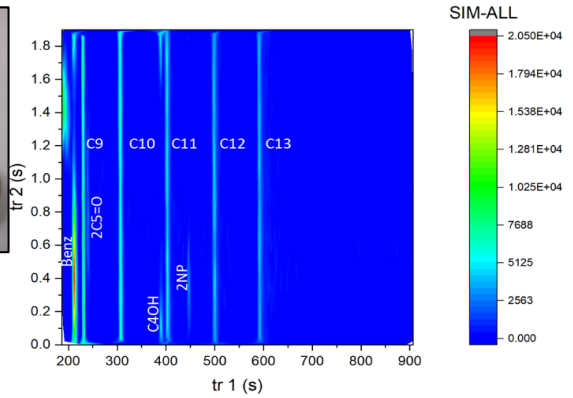
- Amenable to UAV deployment- similar Sandia sensors have been proven in this role.
- Easily fabricated into hand-portable or extremely low power, leave-behind sensors.
  - Allow for long-term fence line monitoring of chemical plants, wells, or pipelines.

Natural Gas Monitoring Micro Sensors- Dept. 8634









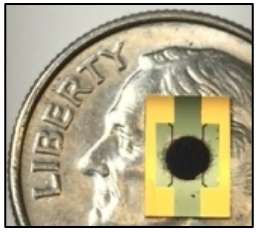
Micro Gas Chromatography (GC or GCxGC)

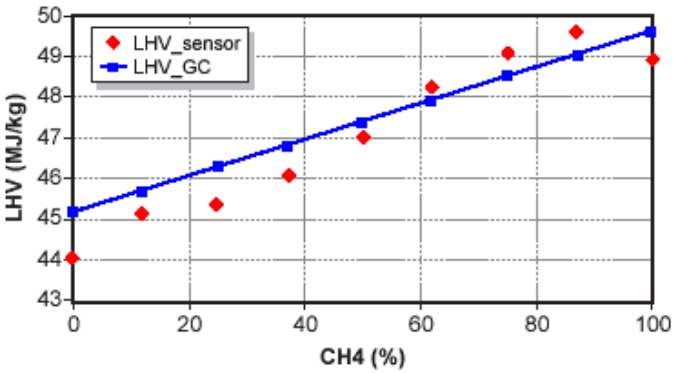
Allows:

- GC separates NG mixture constituents and permanent gasses ($Ar/CO_2/O_2/N_2$).
- GCxGC allows full characterization of all compounds within a mixture.

Applications:

- True BTU measurement in a portable system.





Catalytic Micro-Combustion Sensor

Allows:

- Direct measurement of fuel heating values.
- Detects combustible species in the field

Applications:

- Pipeline leak monitoring via UAV, hand-portable unit, or emplaced sensor.
- BTU survey at custody/transfer stations.

Early prototype combining GC and Catalytic Sensor technologies into a field-portable system.

Additional Information