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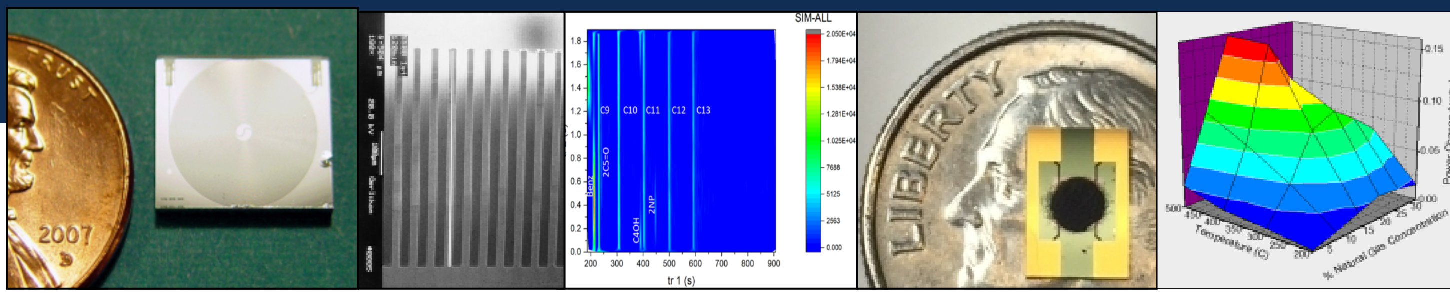

Portable Chemical Detection Systems for Chemicals and Natural Gas

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Dept. 08634

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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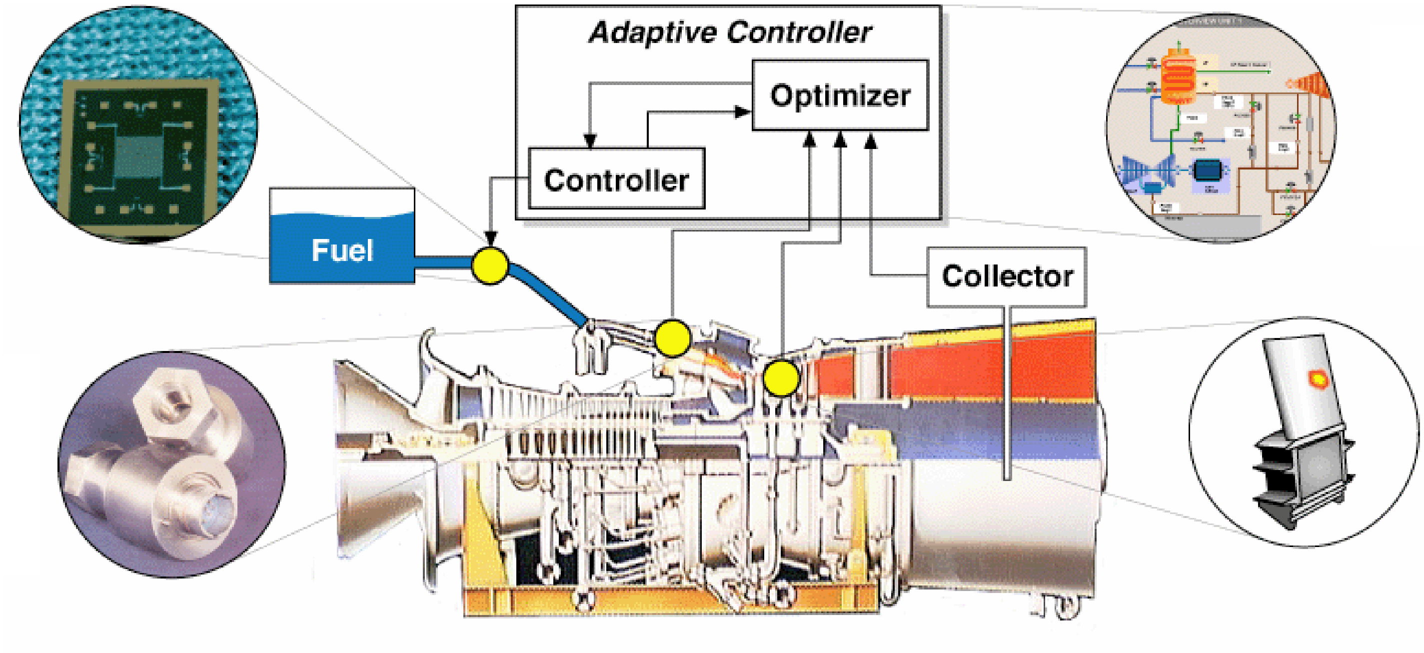
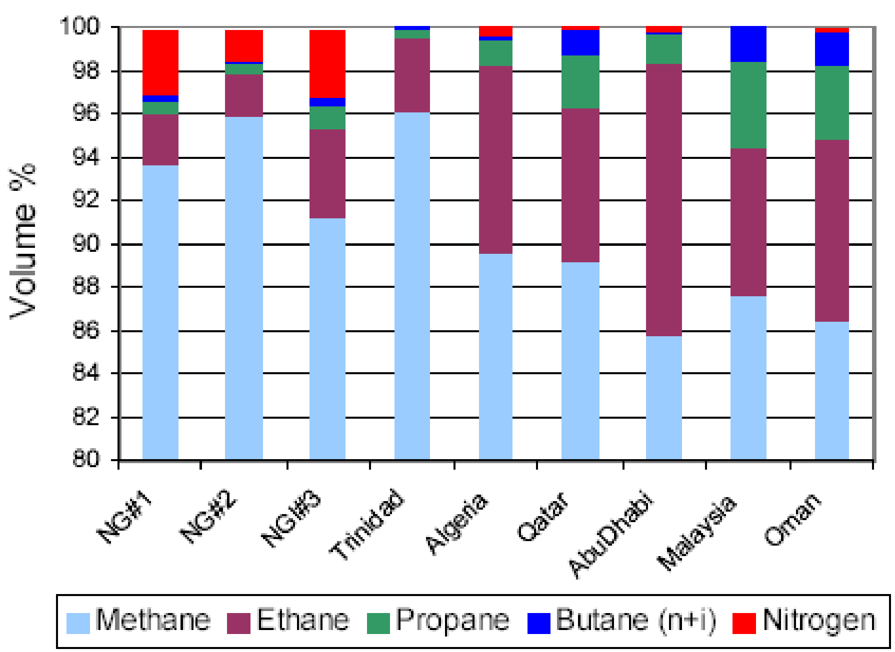
Work Motivation



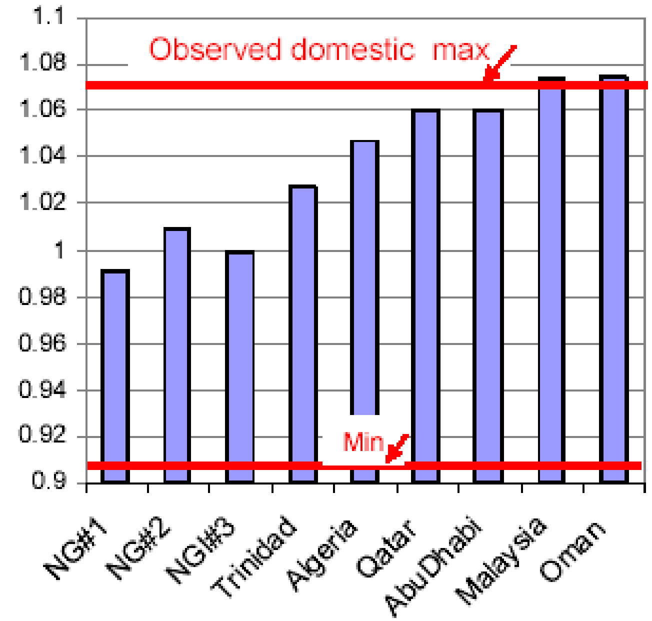
- Combustion efficiency increases can result in significant cost savings for the power generation industry.
- GC/FID/TCD analysis is not rapid enough to measure lower heating value (LHV) or Wobbe Index real time
  - To address this technical shortcoming Sandia sought to invent a faster sensor.
- Other 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

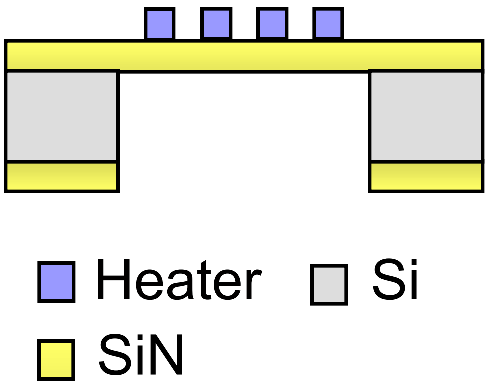
Descriptor - include initials, /org#/date

Slide courtesy of George Richards at NETL

Microhotplate Devices

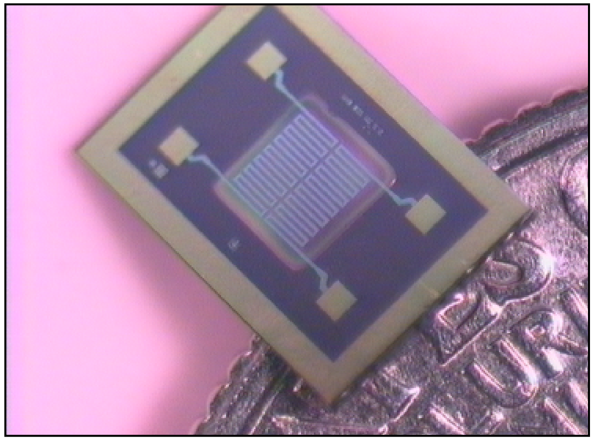
Device:

- 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.

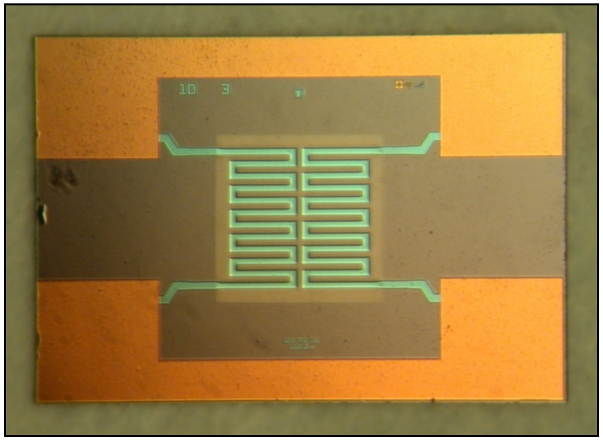


Performance:

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



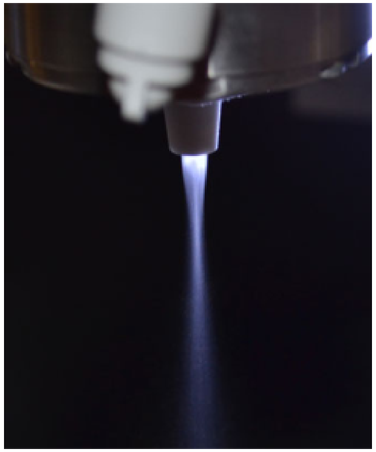
Early Microhotplate Design

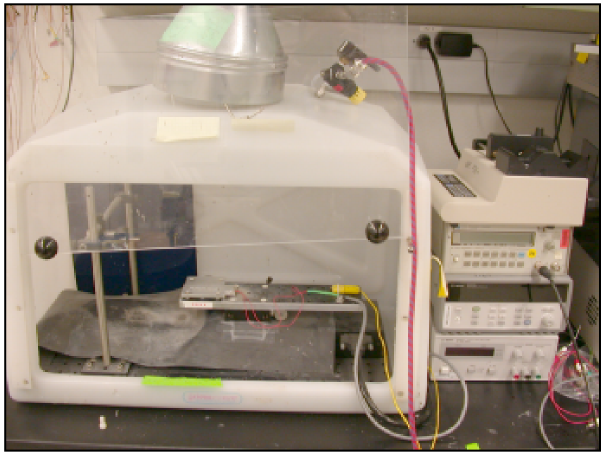


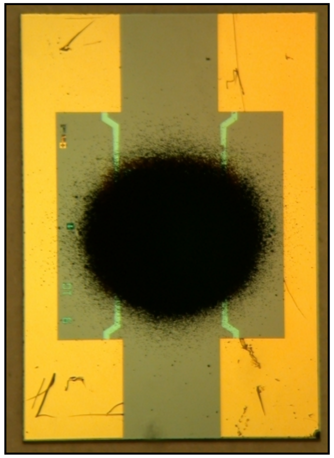
Current Calorimeter Design

Sensor Preparation and Operation

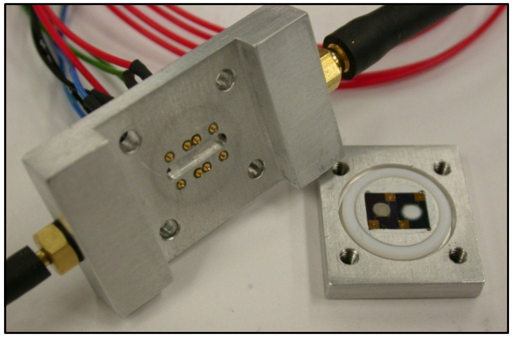
- Temperature-controlled stage aids pattern control and film definition
- Ultrasonic nebulizer with a robotic stage applies catalyst spot to microhotplate.





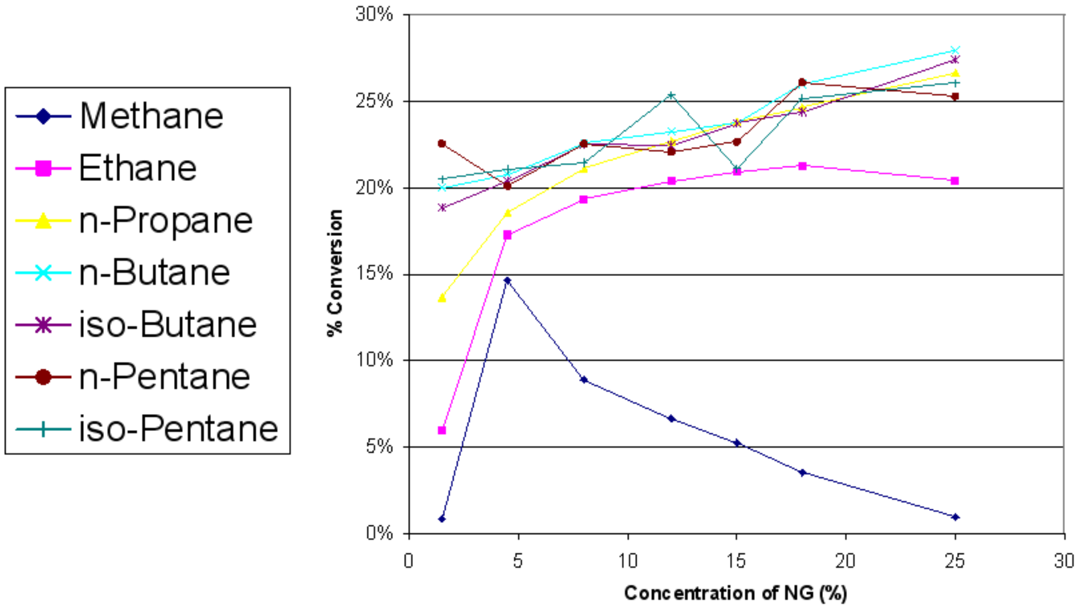


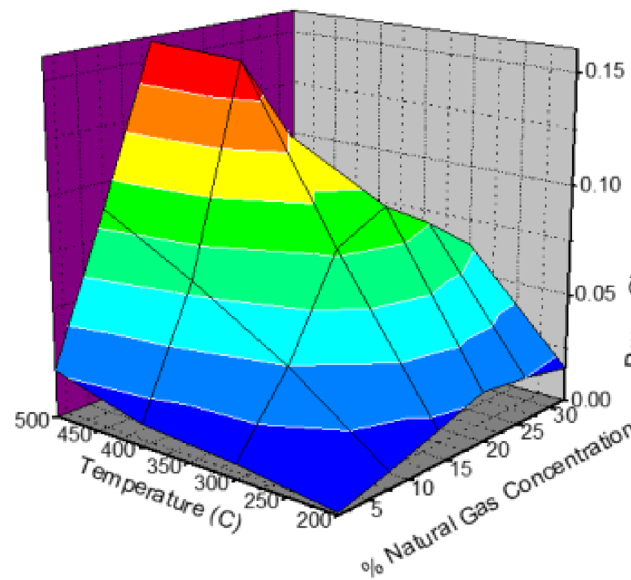
- Sensor fixture allows inclusion of a reference microhotplate that compensates for environmental drift.
- Temperature control circuitry monitors combustion of NG on catalyst spot.
  - This constitutes the sensor's signal.



Combustion Product Analysis

400 °C Hotplate Temp.





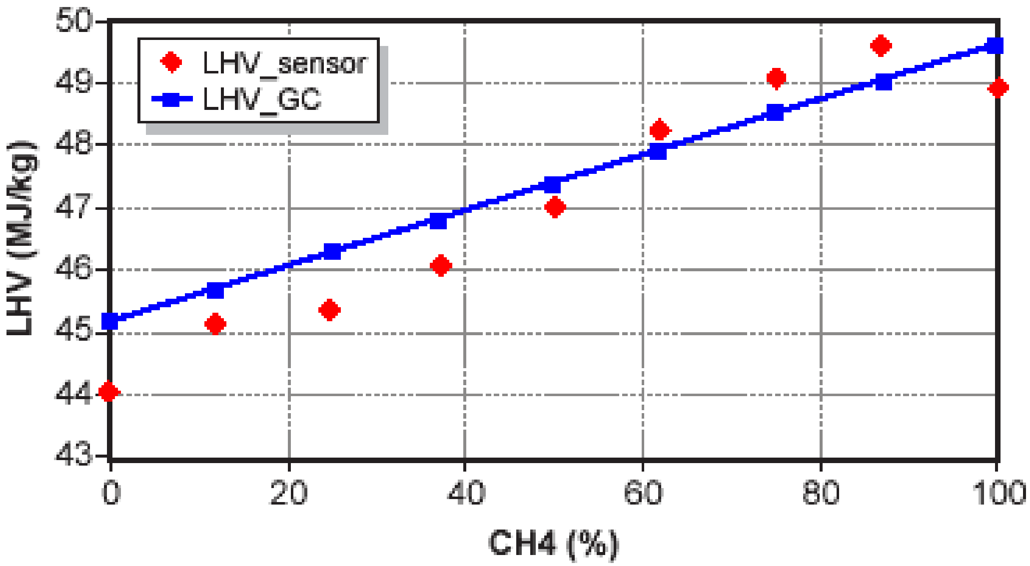
- Large differences in conversion and speciation noted as a function of flow, catalytic micro-combustor temperature, and NG composition.
- Competition for catalytic combustion sites contributes to measurement error.

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

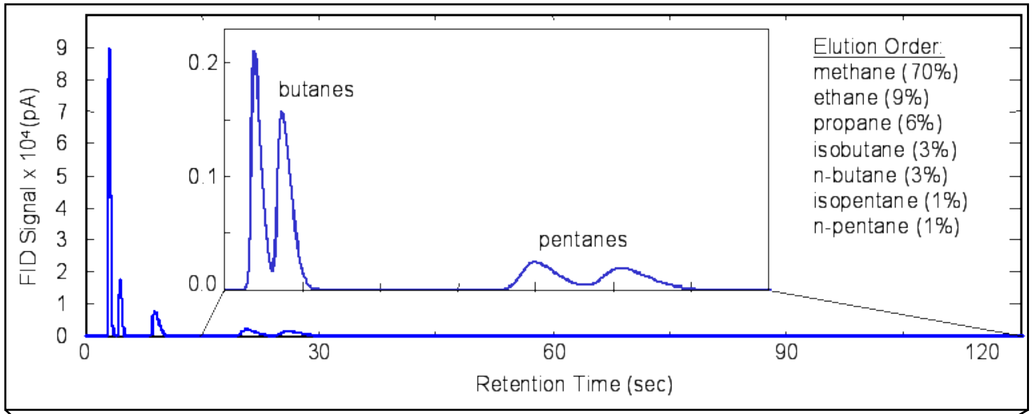
Field test sensor signal vs. reference measurement

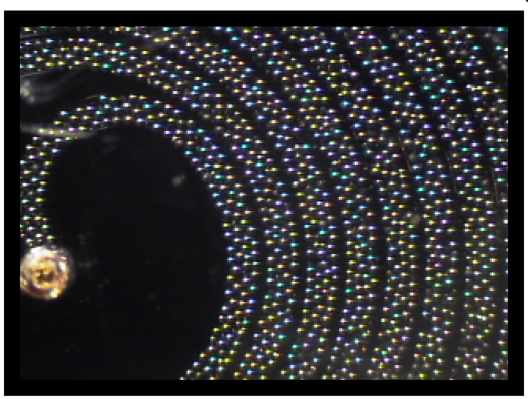


The LHV value is determined by using proprietary sensor calibration factors to associate signal with LHV content.

- 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

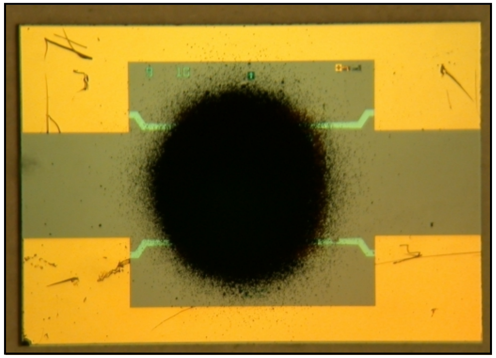




µGC Separation

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.

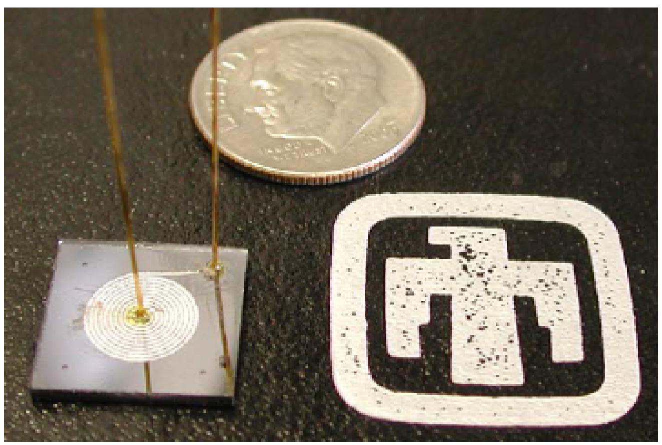


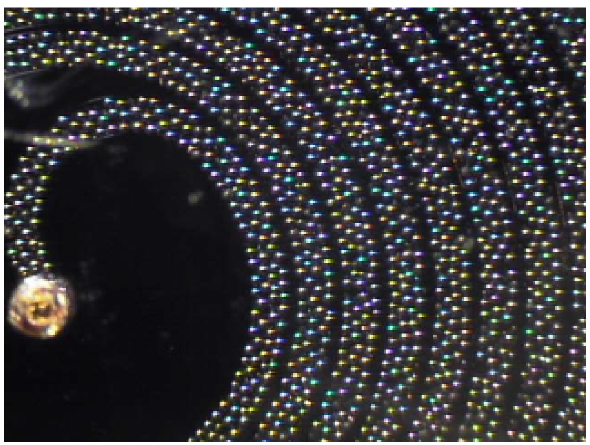
Catalytic Micro-Combustor

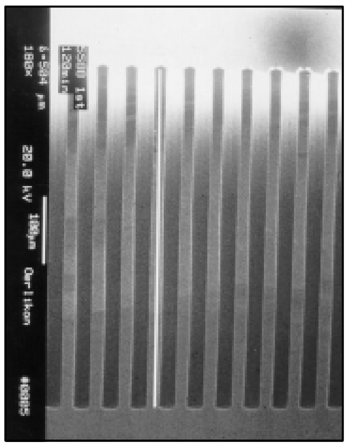
Micro Gas Chromatography (μGC) Technology

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

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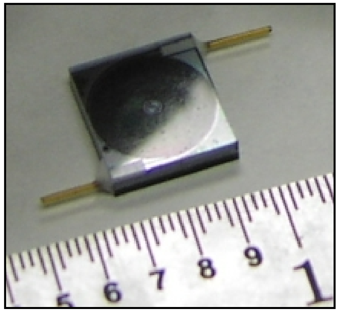
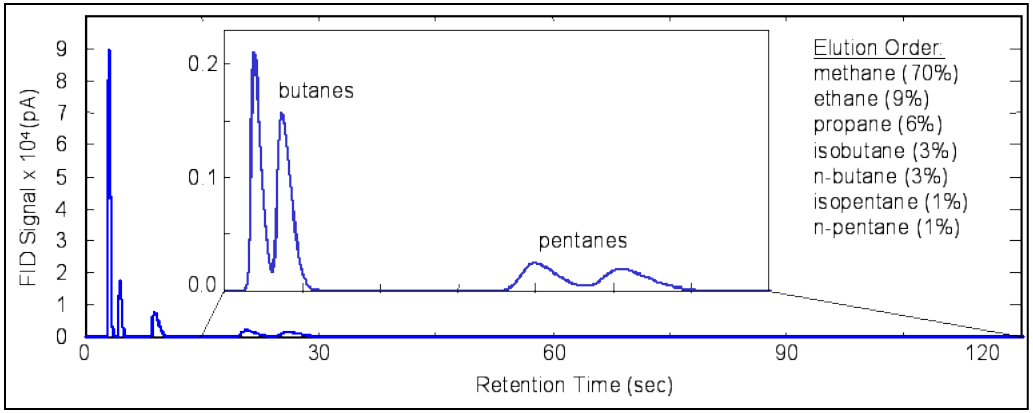
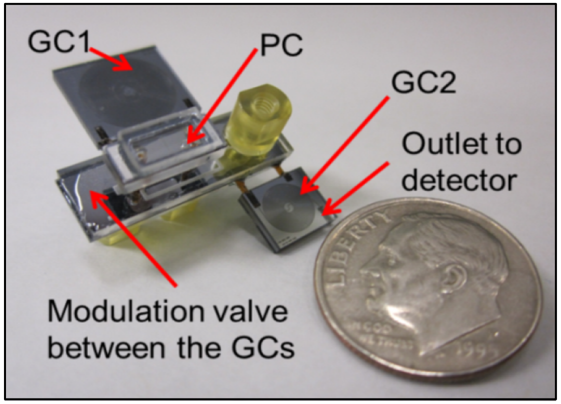
Sandia has miniaturized this technology and produced both μGC and μGC x μGC systems for analysis of complex chemical mixtures.

- Useful for NG and petrochemical analysis.

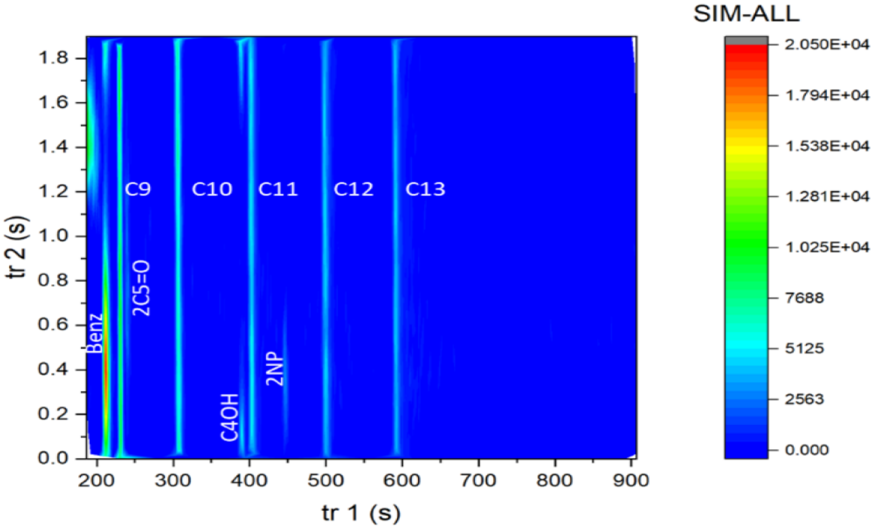


Packed μGC with commercial materials.



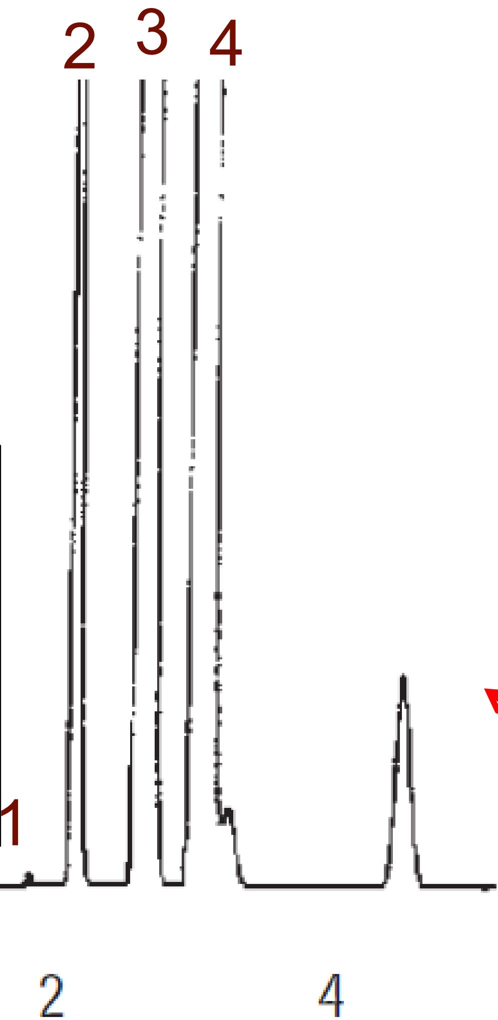


μGC x μGC



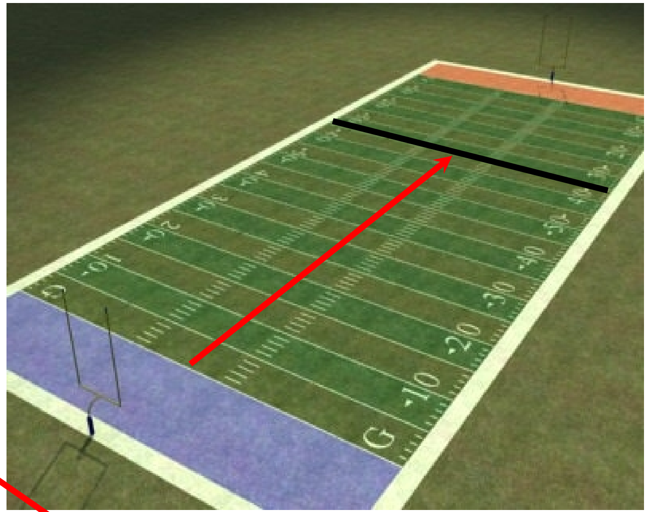
Unique µGC Materials Technology

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

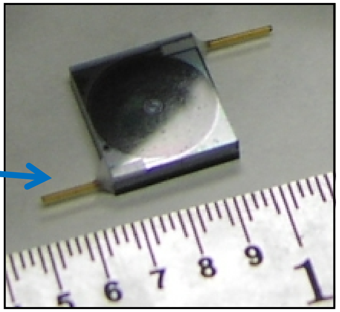


Chromatogram for 60m RTX-1 GC column from Restek Archive: www.restek.com

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

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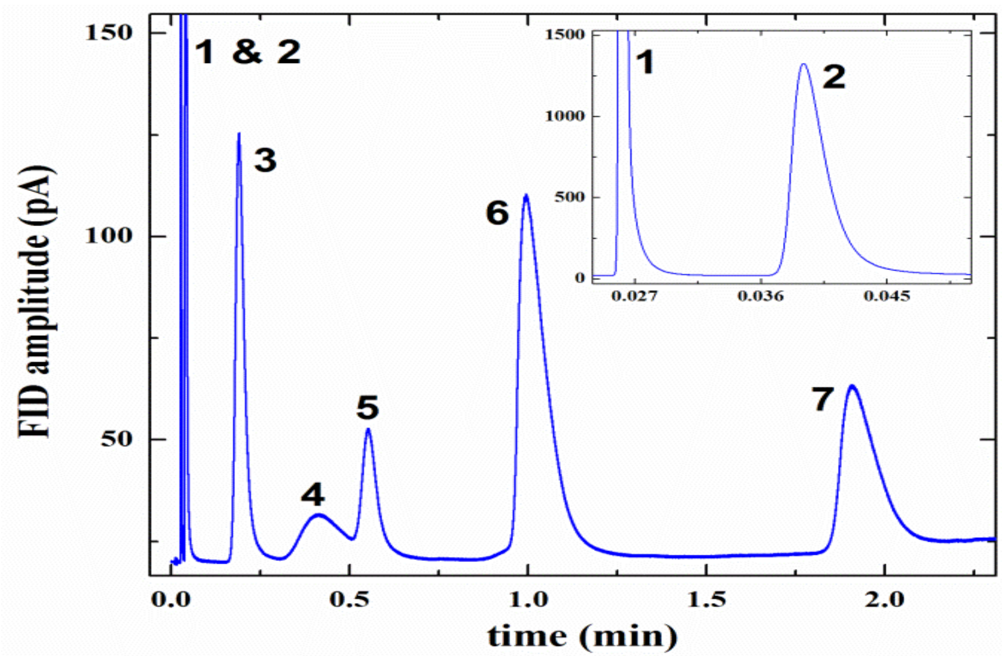
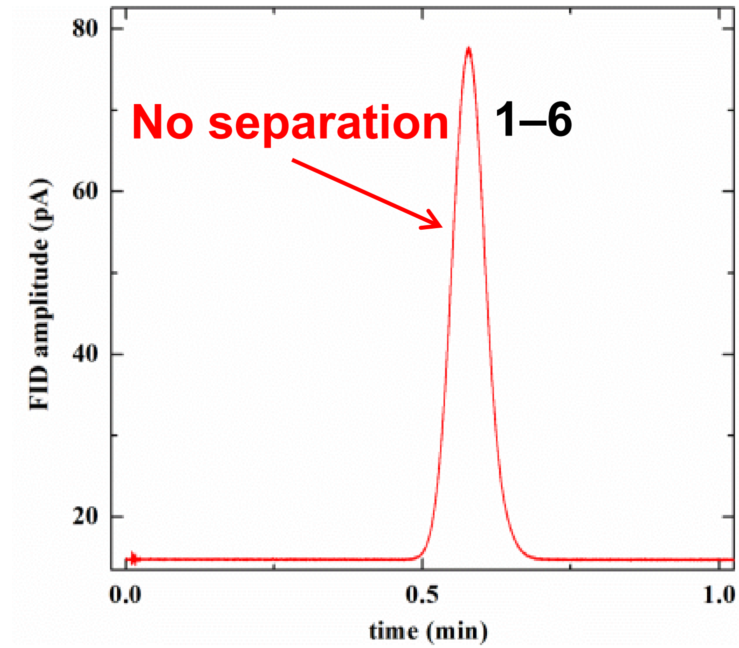
MOF thin film, *µ*GC natural gas separation.



*µ*GC 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

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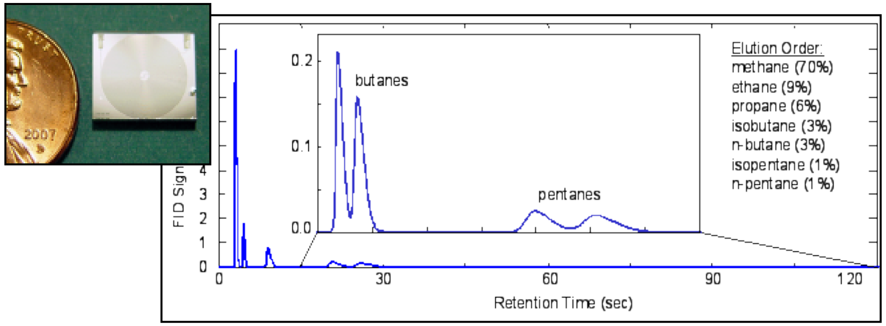
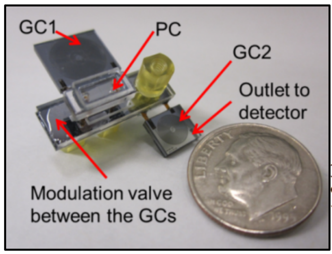
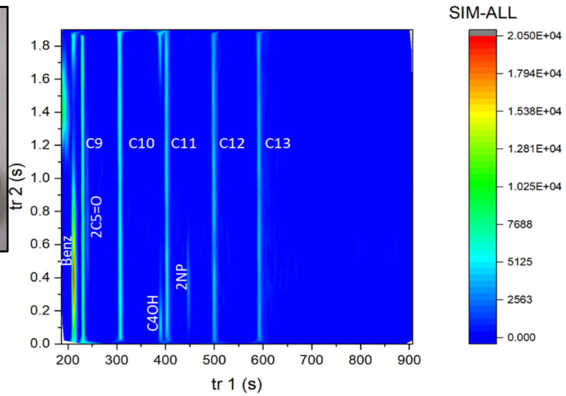






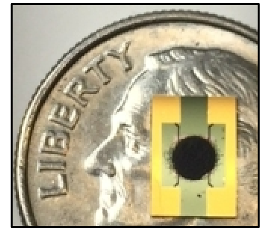
Micro Gas Chromatography (GC or GCxGC)

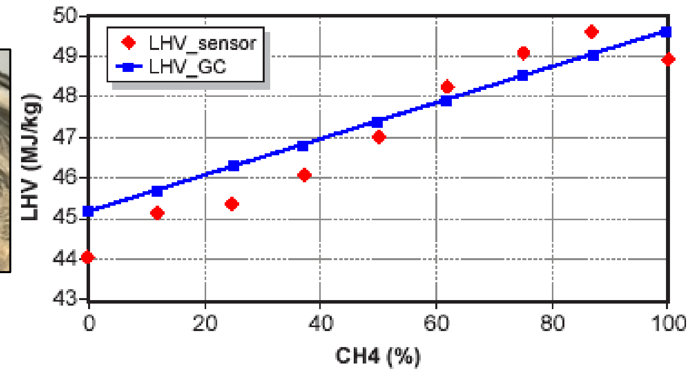
Allows:

- 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.