# Cavity-Enhanced Gas Analyzer for Process Control Applications

DOE SBIR Phase II
DE-FG02-03ER83849
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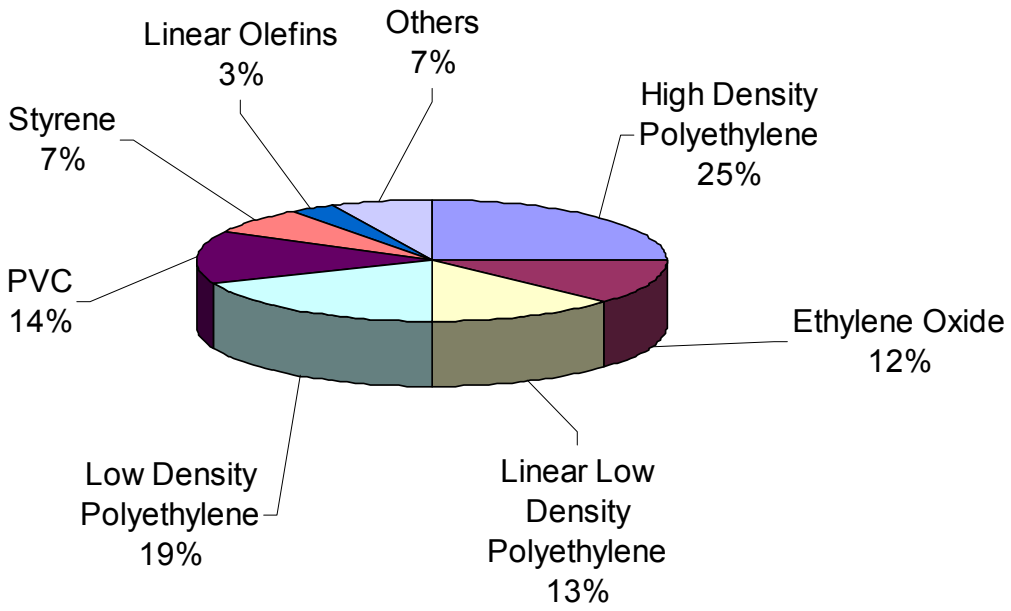
# Outline

- Motivation
- Application addressed in SBIR effort
- Proposed Solution:  Off-Axis ICOS
- Summary of Phase I Results
- Phase II Results
- Commercialization Potential
- Acknowledgments

# Motivation

## Ethylene is the most widely produced petrochemical

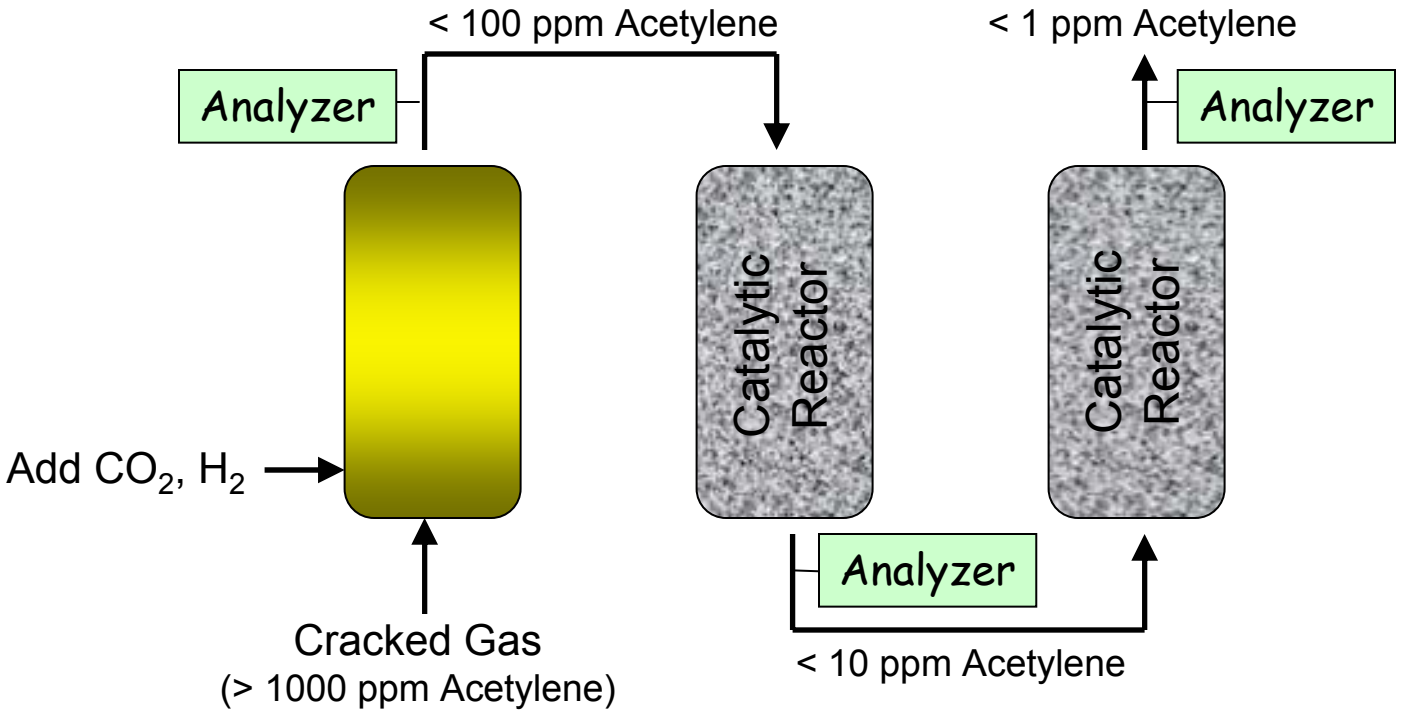



**Ethylene-Based Products**

- > 90M tons/year
- ~$18B market
- Major Producers
  - Dow (9.3 %)
  - ExxonMobil (7.1 %)
  - Shell (5.4 %)
  - Equistar (4.7 %)
  - BP (4.1 %)
  - Sinopec (3.9 %)

# Application

## Acetylene contamination in ethylene




- Polymer-grade ethylene must contain <10 ppm acetylene
- Actively control hydrogenation to minimize acetylene and ethane
- In the event of an acetylene upset (>1000 ppm), rapidly divert stream to prevent contamination of catalysts and stored product

**Need fast (~5 seconds), sensitive (< 1 ppm) measure of acetylene in ethylene**

# Current Technology

## Gas Chromatography (GC)

- Accepted industry standard
- Sufficiently sensitive (< 1.0 ppm acetylene)
- Too slow (~2 minutes/measurement)
- Expensive (cost of ownership ~$300k over 15 years per GC)

**Desire much faster analyzer with comparable sensitivity at a lower price**

# Alternative Technologies

## Evaluated by Dow Chemical Company

- Miniature Gas Chromatography
  - Still too slow (40 seconds/analysis)
  - Early development stage

- Mass Spectrometry
  - Expensive
  - Insufficiently robust

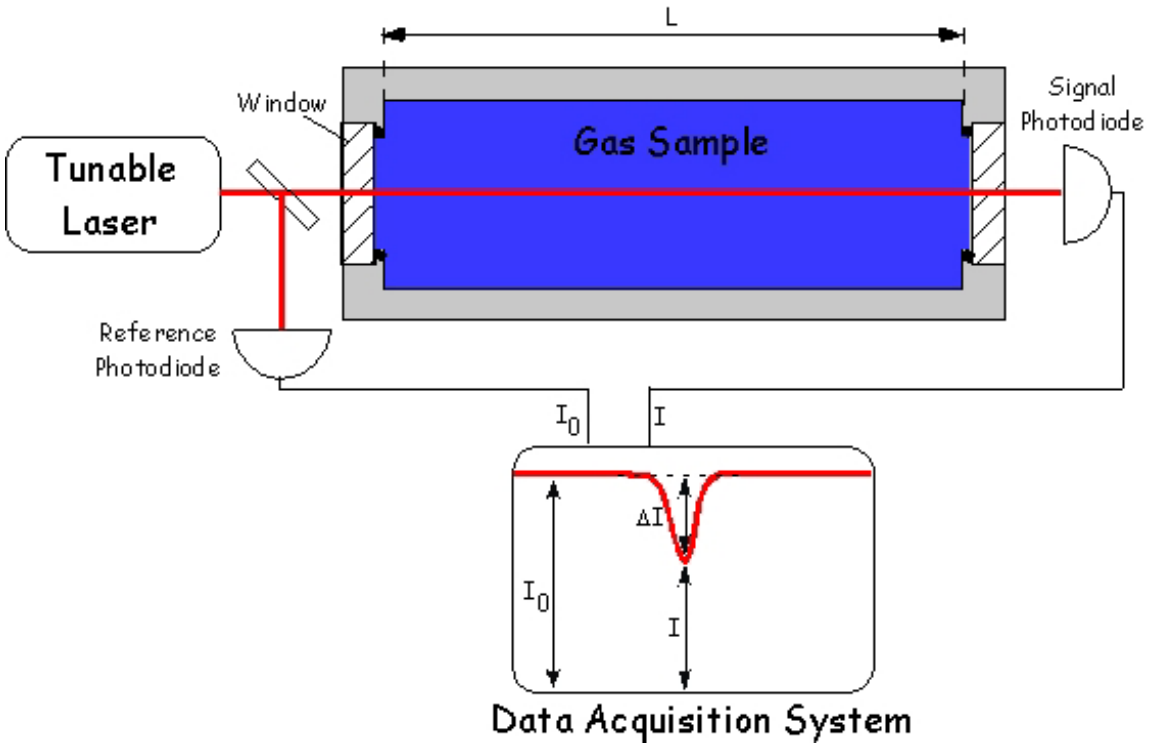
- Non-Dispersive Infrared (NDIR)
  - Insufficient sensitivity
  - Cannot distinguish between different flow constituents

- Fourier-Transform Infrared (FTIR)
  - Insufficient sensitivity
  - Expensive

- Laser Absorption Spectroscopy (TDLAS)
  - Dow Laser Spectroscopy Workshop
  - **Very promising!**

# Absorption Spectrometry

## Overview



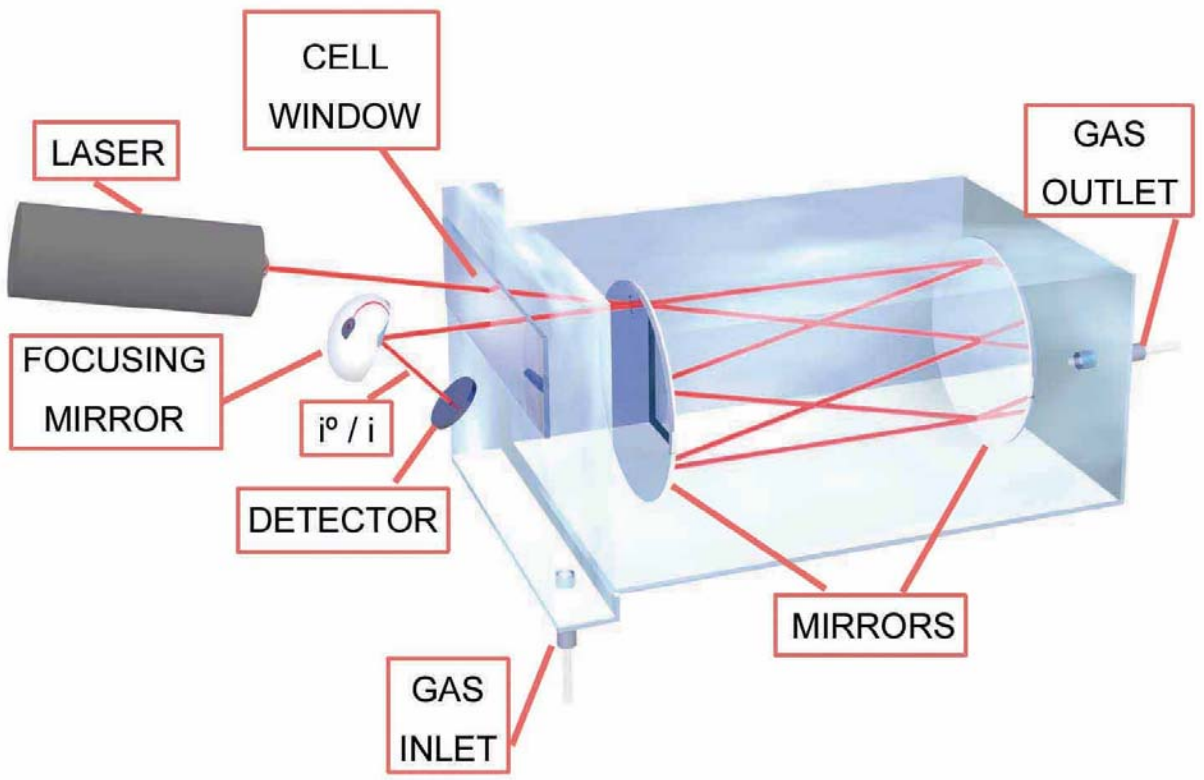

Beers Law: $\Delta I/I_o = 1-\exp(-\alpha L)$

- Absorption spectrometry is a direct measure of concentration
- Very selective - $C_2H_2$ absorbs light between 1510 - 1545 nm
- Fast – laser can be reproducibly swept at > 100 Hz
- For a 1 meter sample containing 100 torr of 1 ppm acetylene, $\Delta I/I_0 \sim 10^{-5}$

**Single pass absorption spectrometry is not sufficiently sensitive**

# Absorption Spectrometry

## Multipass Methods

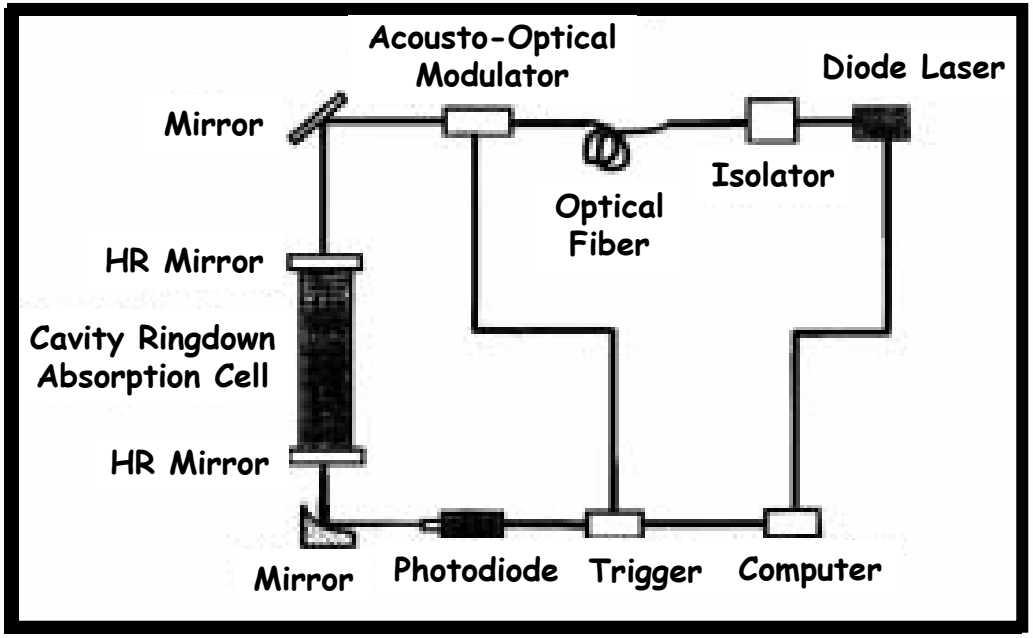


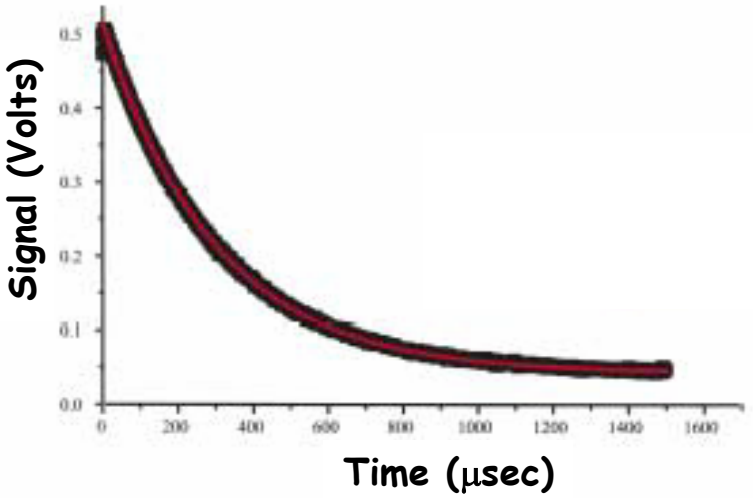

- Increase pathlength (x 100) by bouncing light between mirrors 100 times
- Single-pass $\Delta I/I_0 \sim 10^{-5} \rightarrow$ Multipass $\Delta I/I_0 \sim 10^{-3}$ (still a small absorption)
- Very sensitive to alignment – beam must pass precisely through holes
- Several manufacturers attempted and failed to meet Dow's sensitivity requirements

**Multipass absorption methods are inadequate for this application**

# Absorption Spectrometry

## Cavity Ringdown Spectroscopy



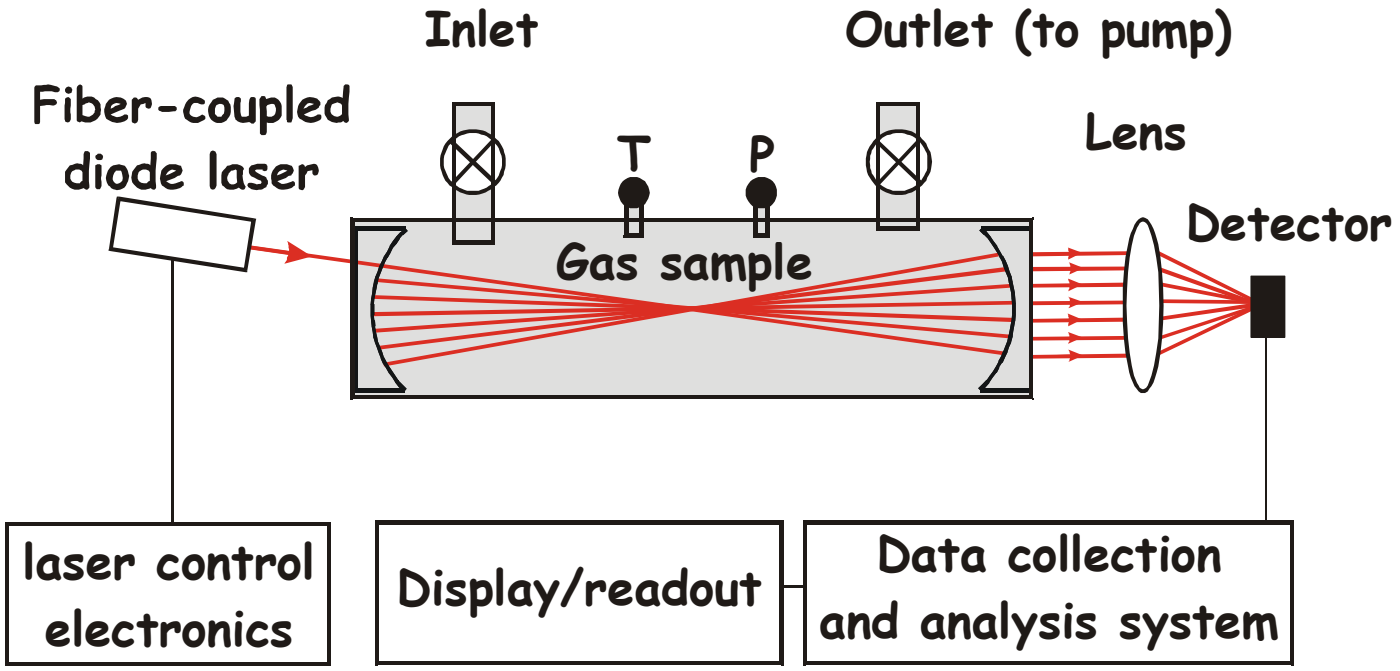




- Developed by Anthony O'Keefe (CEO, Los Gatos Research) in 1988
- Couple light into the cavity in a constrained alignment ("mode-matched")
- Rapidly shut-off laser and measure the rate of decay of light from the cavity
- Decay time, $\tau$, is proportional to losses within the cavity: $\tau = L/[c*(1-R+A)]$
- Very sensitive to alignment and requires expensive components (fast electronics, AOM)
- Difficult to implement in samples with relatively high loss (petrochemical applications)

**Cavity ringdown is insufficiently robust and suboptimal in lossy media**

# Off-Axis ICOS

## Ultrasensitive cavity-enhanced absorption

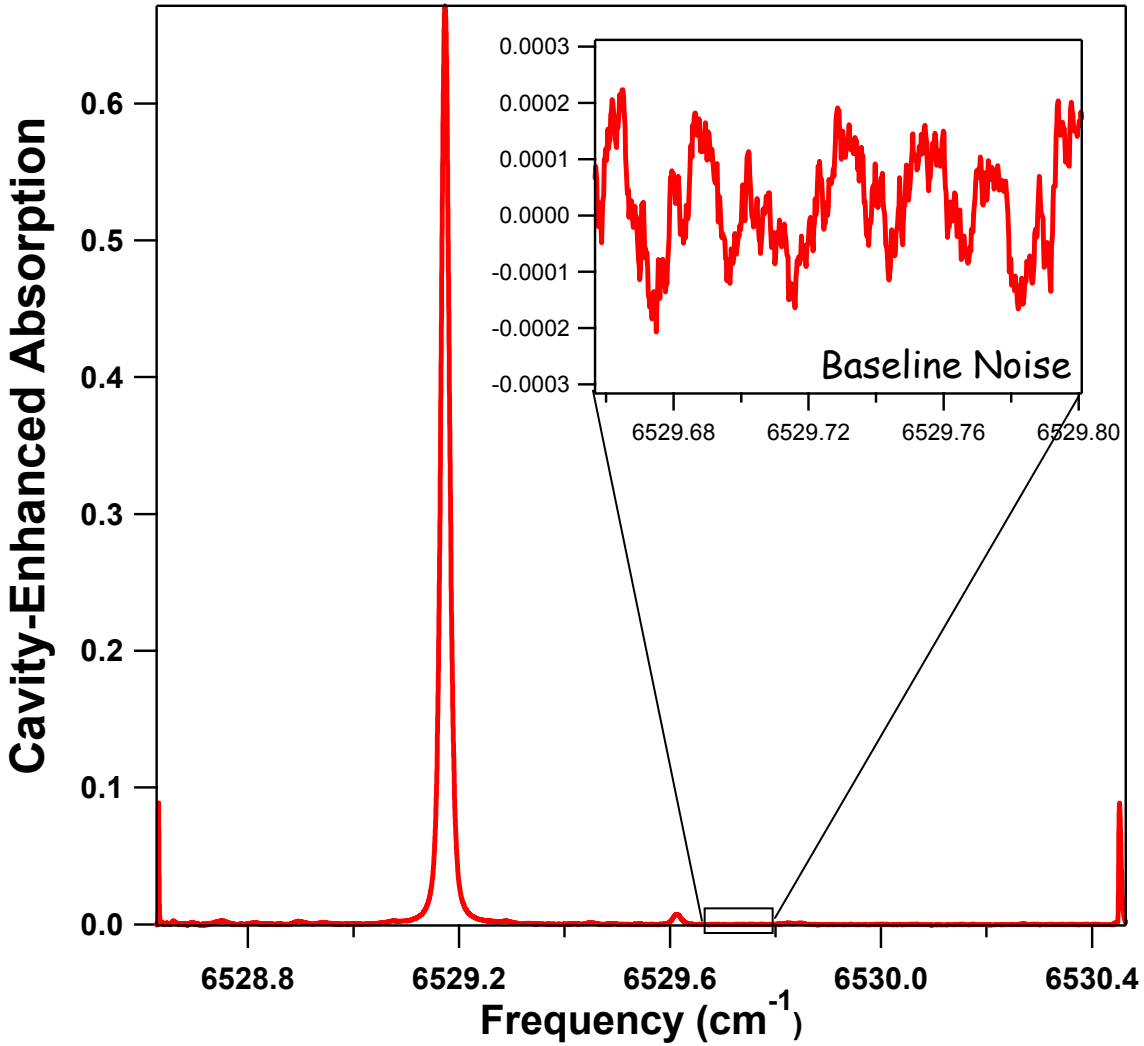



- Off-Axis ICOS was developed by Los Gatos Research over last 3 years
- Sample contained in optical cavity comprised of 2 highly reflective mirrors (R > 99.99%)
- Light enters and exits cavity by passing *through* the mirrors
- Increase pathlength by $(1\text{-}R)^{-1}$ ~ 10,000 times, giving several kilometers of effective path
- Single-pass $\Delta I/I_0 \sim 10^{-5} \rightarrow$ Multipass $\Delta I/I_0 \sim 10^{-1}$ (a considerable absorption)
- Not sensitive to alignment – exact beam path not critical

**Off-Axis ICOS provides unheralded sensitivity in a robust package**

# Summary of Phase I Results

## Off-Axis ICOS has Sufficient Sensitivity

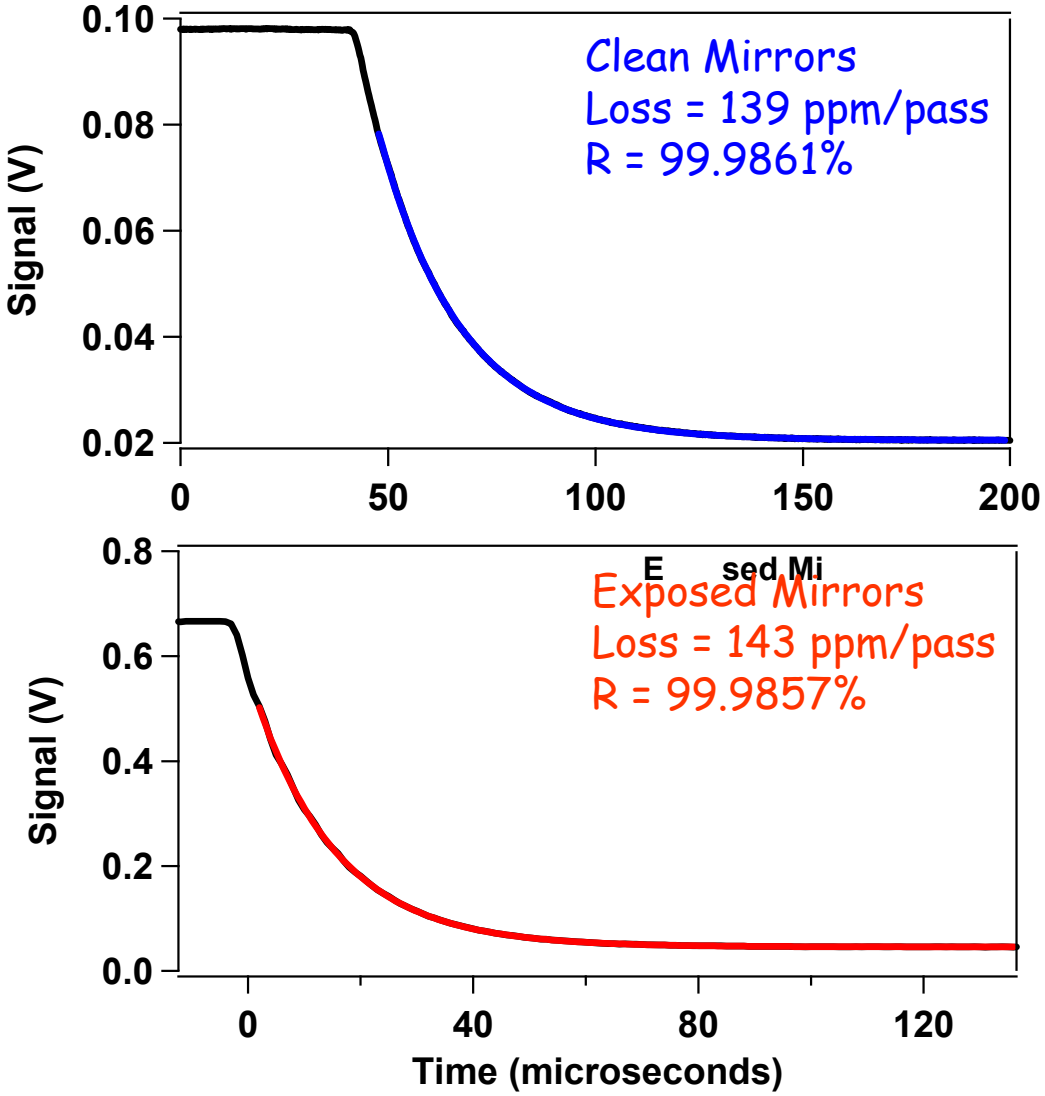



- 10.4 ppm Acetylene/$N_2$
- S/N ~ 3500:1 in 10 seconds
- Can detect < 10 ppb
- Per-pass absorption ~ $10^{-4}$

**Off-Axis ICOS analyzer can readily detect less than 1 ppm acetylene**

# Summary of Phase I Results

## Mirrors do NOT degrade over 6 months



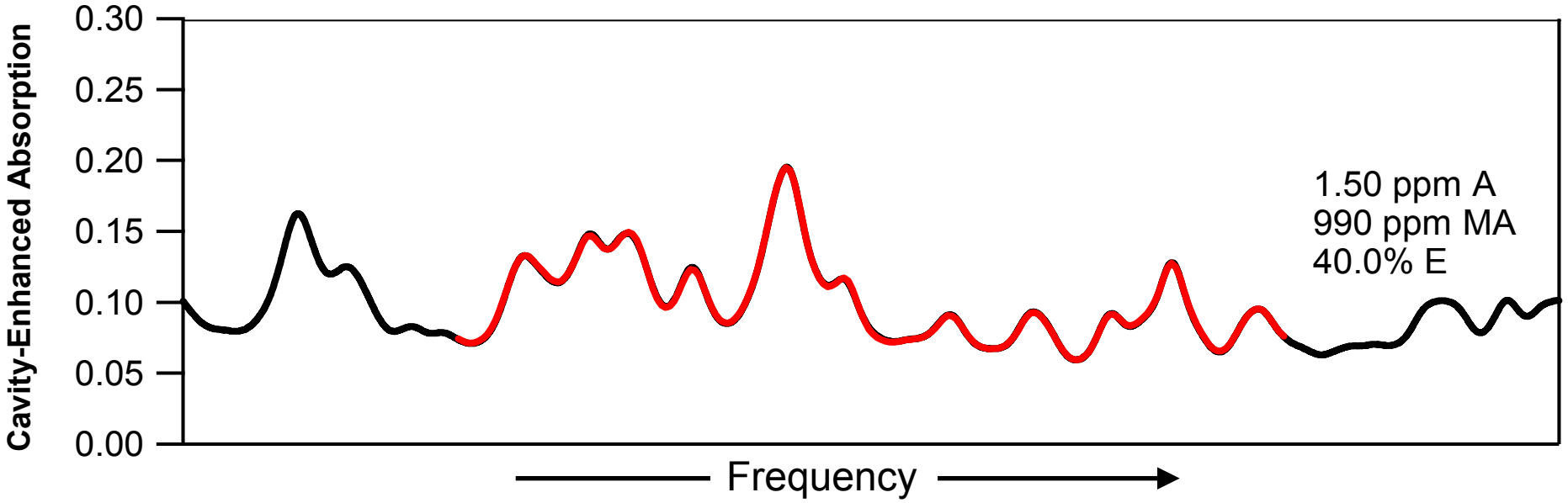

Mirrors tested using cavity ringdown

- Rapidly shutoff laser
- Measure exponential light decay
  $I(t) = \exp(-t/\tau)$
- Decay rate proportional to loss
  $\text{Loss} = L / (c\tau)$
- Clean Mirrors R = 99.9861%
- Exposed Mirrors R = 99.9857%

**No significant mirror degradation after 6 months of exposure!**

# Summary of Phase I Results

## Developed Quantitative Analysis Routine

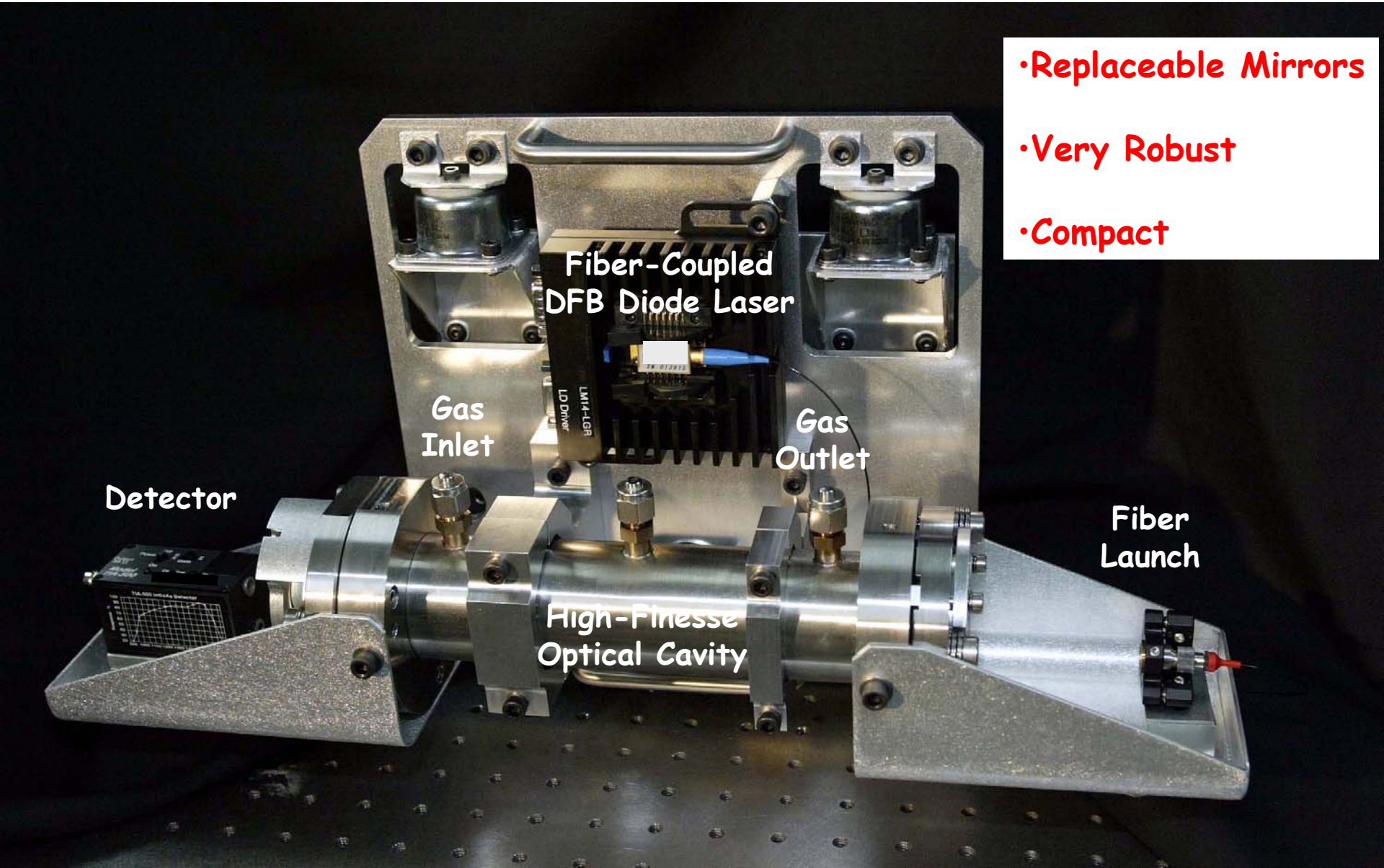



| | Mixture 1 | | Mixture 2 | | Mixture 3 | |
|---|---|---|---|---|---|---|
| | **GC** ±0.1 ppm 120 seconds | **Off-Axis ICOS** ±0.1 ppm 2 seconds | **GC** ±0.1 ppm 120 seconds | **Off-Axis ICOS** ±0.1 ppm 2 seconds | **GC** ±0.1 ppm 120 seconds | **Off-Axis ICOS** ±0.1 ppm 2 seconds |
| **Acetylene** | **8.0 ppm** | **7.87 ppm** | **1.50 ppm** | **1.52 ppm** | **1.48 ppm** | **1.47 ppm** |
| **Methyl Acetylene** | **999 ppm** | **957 ppm** | **990 ppm** | **962 ppm** | **5144 ppm** | **5655 ppm** |
| **Ethylene** | **40.1 %** | **41.6 %** | **40.0 %** | **40.8 %** | **40.0 %** | **44.7 %** |

**OA ICOS acetylene analyzer successful for realistic ethylene flows**

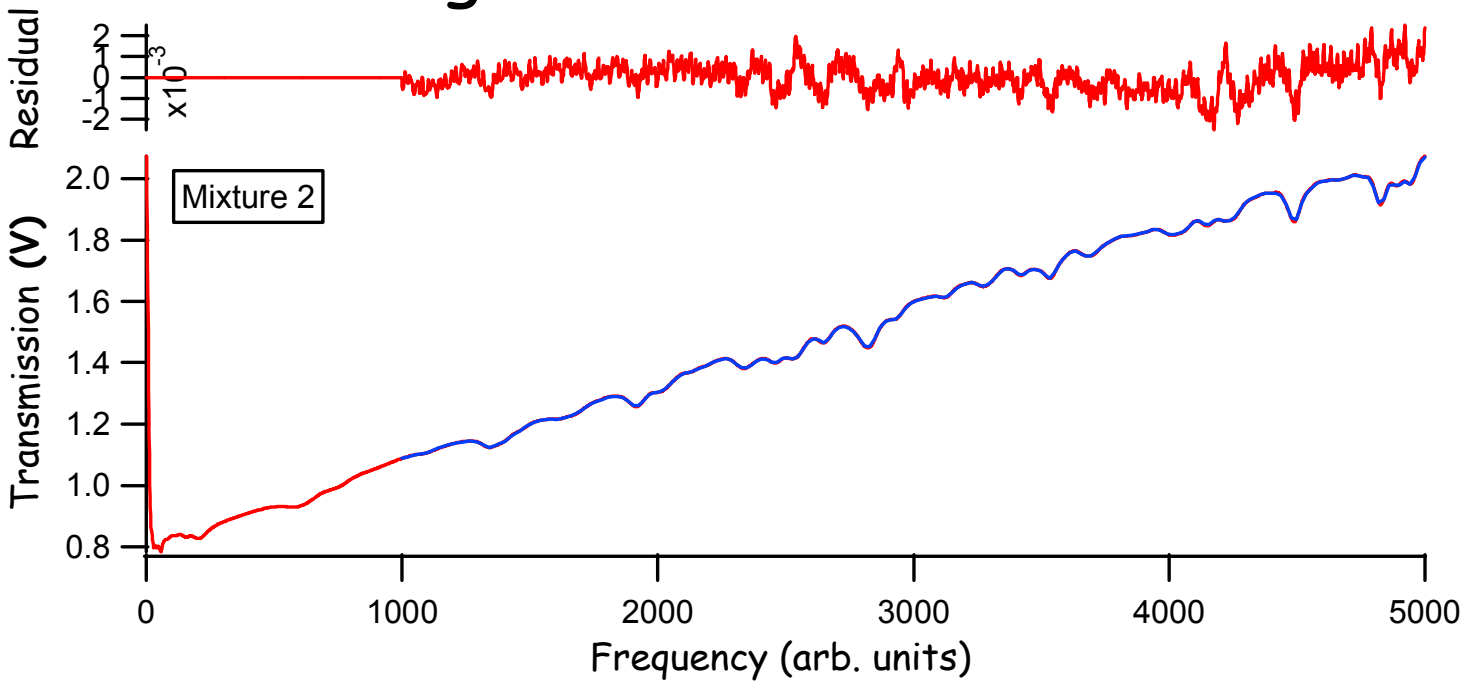
# Phase II Results

## Designing the Phase II Instrument



# Phase II Results

## Testing the Phase II Instrument




| | Mixture 1 | | Mixture 2 | | Mixture 3 | |
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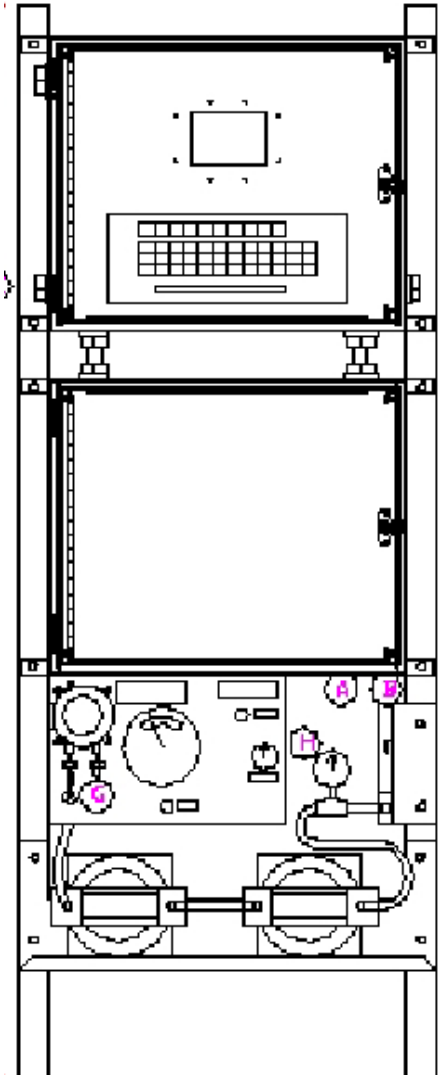
| | **GC** ±0.1 ppm 120 seconds | **Off-Axis ICOS** ±0.1 ppm 2 seconds | **GC** ±0.1 ppm 120 seconds | **Off-Axis ICOS** ±0.1 ppm 2 seconds | **GC** ±0.1 ppm 120 seconds | **Off-Axis ICOS** ±0.1 ppm 2 seconds |
| **Acetylene** | **8.0 ppm** | **8.16 ppm** | **1.50 ppm** | **1.56 ppm** | **1.48 ppm** | **1.43 ppm** |
| **Contaminant** | **999 ppm** | **955 ppm** | **990 ppm** | **942 ppm** | **5144 ppm** | **5012 ppm** |
| **Ethylene** | | | | | | |

**Phase II Instrument meets requirements in realistic ethylene flows**

# Phase II Results

## Hardware Integration

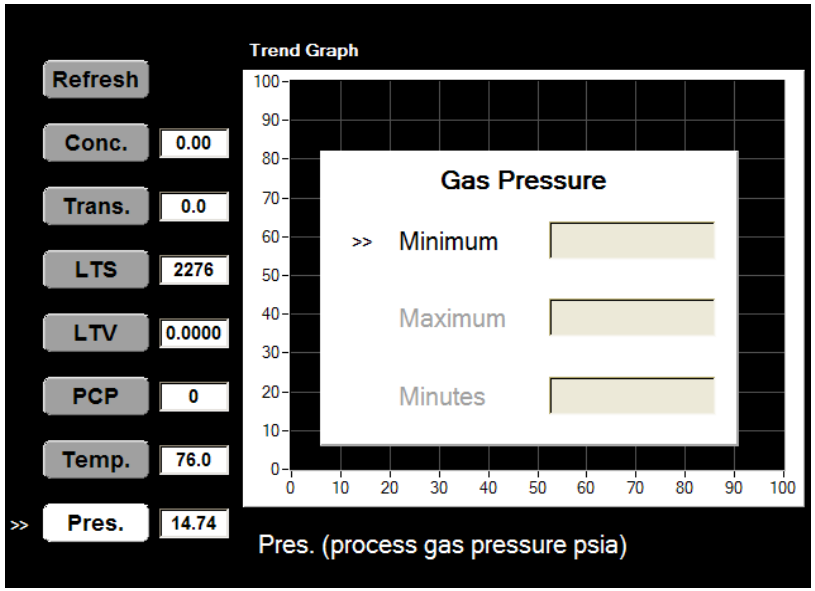



- Electronics
  - Power Supplies
  - Valve Controllers
  - PC/104 Embedded Computer
  - Laser Controller
- Optical Analyzer
  - Off-Axis ICOS Analyzer
  - Heating Blanket
- Gas Handling System
  - Explosion-Proof Vacuum Pumps
  - Flow Controller
  - Gas Regulator

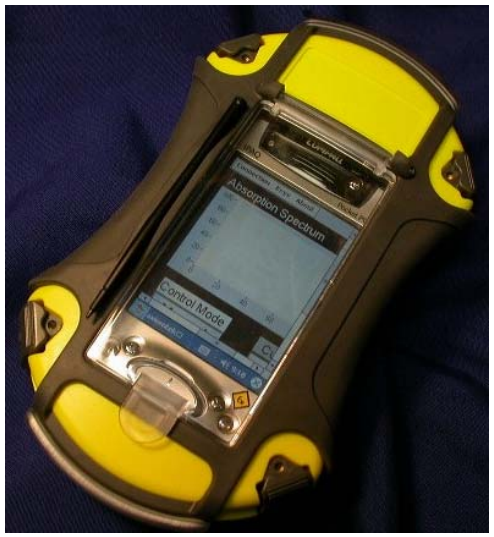
**Off-Axis ICOS analyzer integrated in collaboration with ASI**

# Phase II Results

## Software Integration & Features



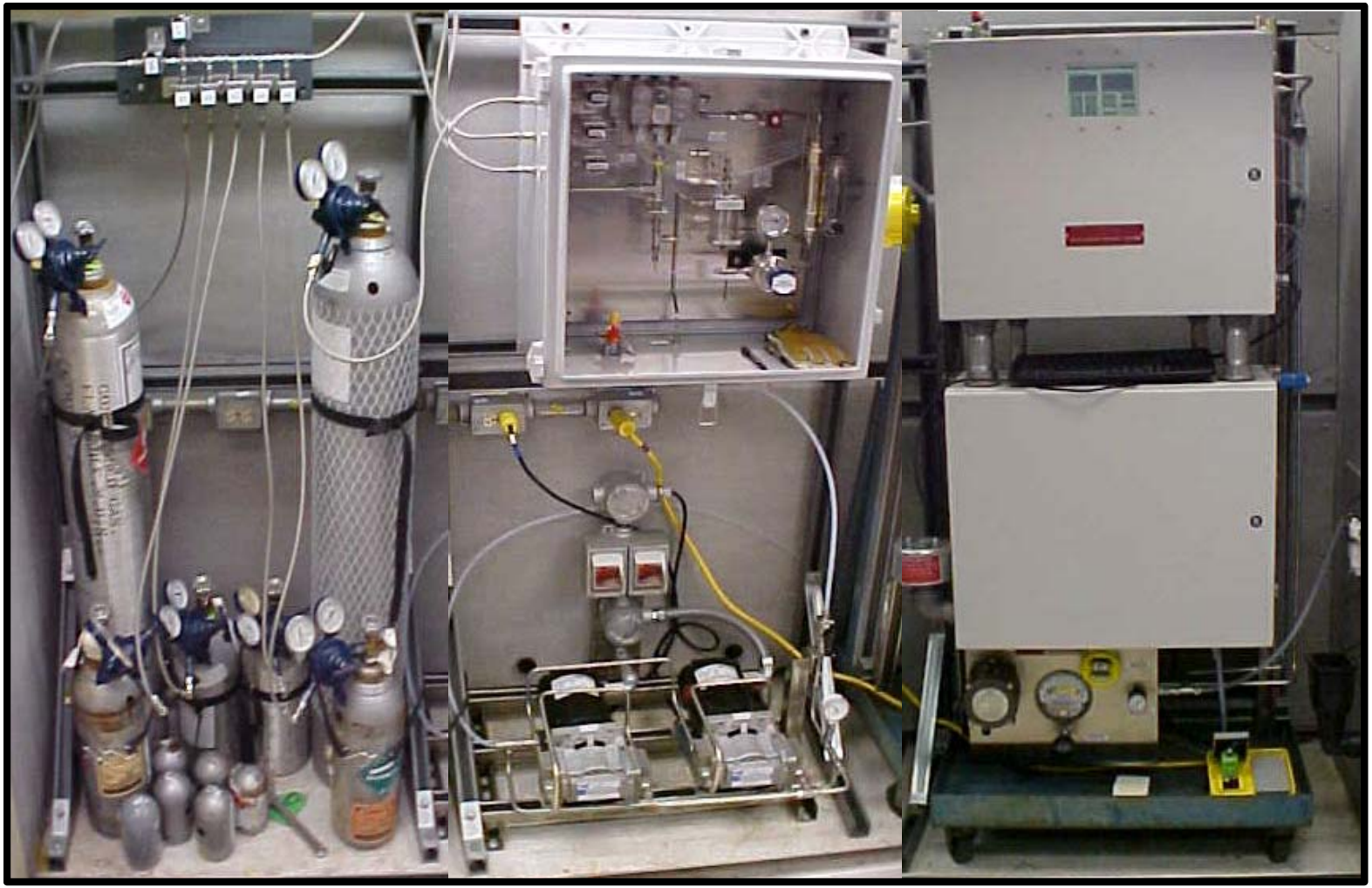

- Software
  - Data Acquisition
  - Laser Control
  - Easy Calibration
- Communication
  - Wireless
  - Ethernet
  - Modbus
  - Fieldbus
  - Profibus
- Safety
  - Automatic diagnostics (SIS/SIL)
  - Zone/Div 1-2, ATEX/CSA/UL




Off-Axis ICOS analyzer integrated in collaboration with ASI

# Phase II Results

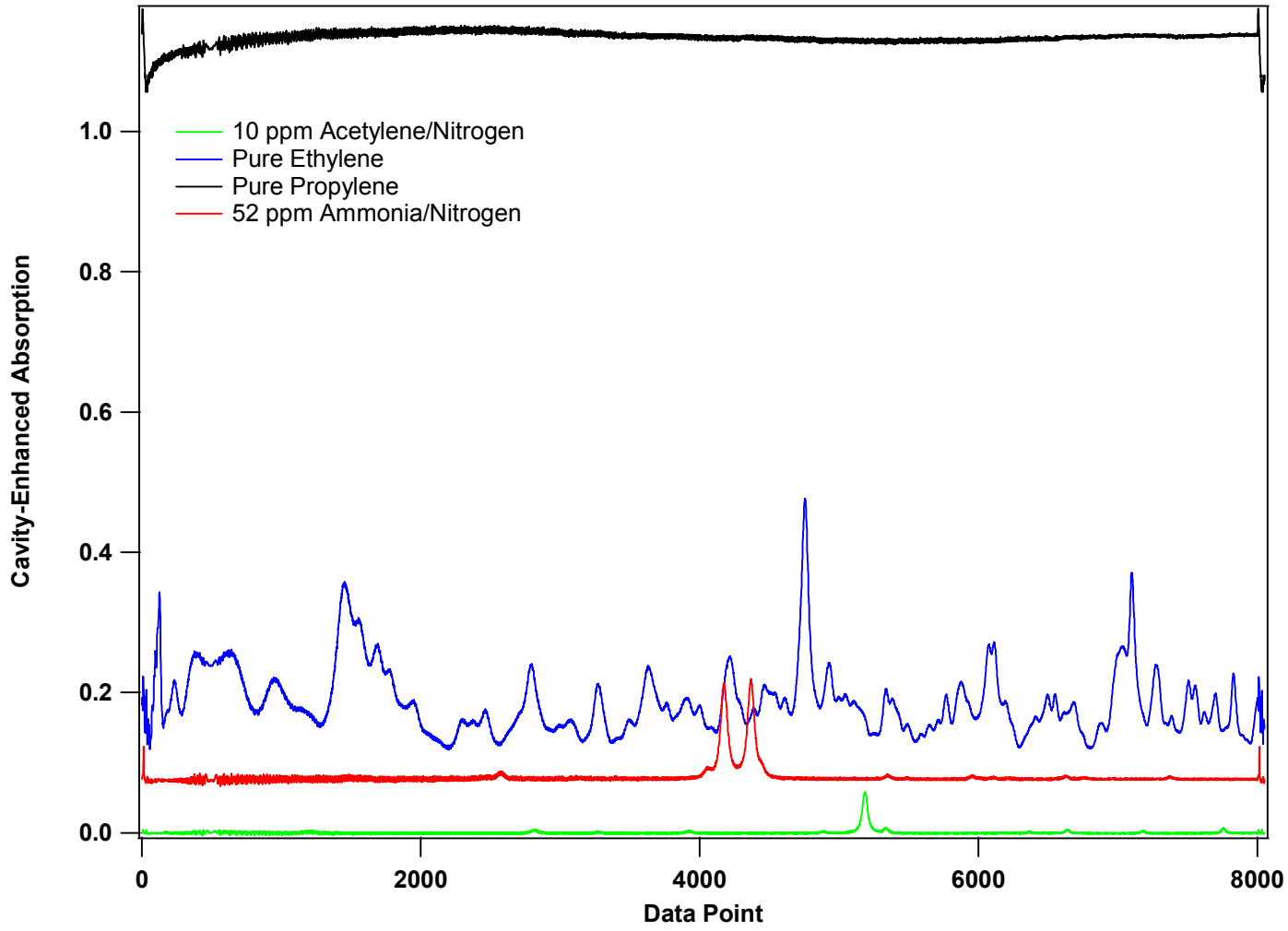
## Installation into Dow Chemical Company Laboratory



**Dow is providing both laboratory and field testing**

# Phase II Results

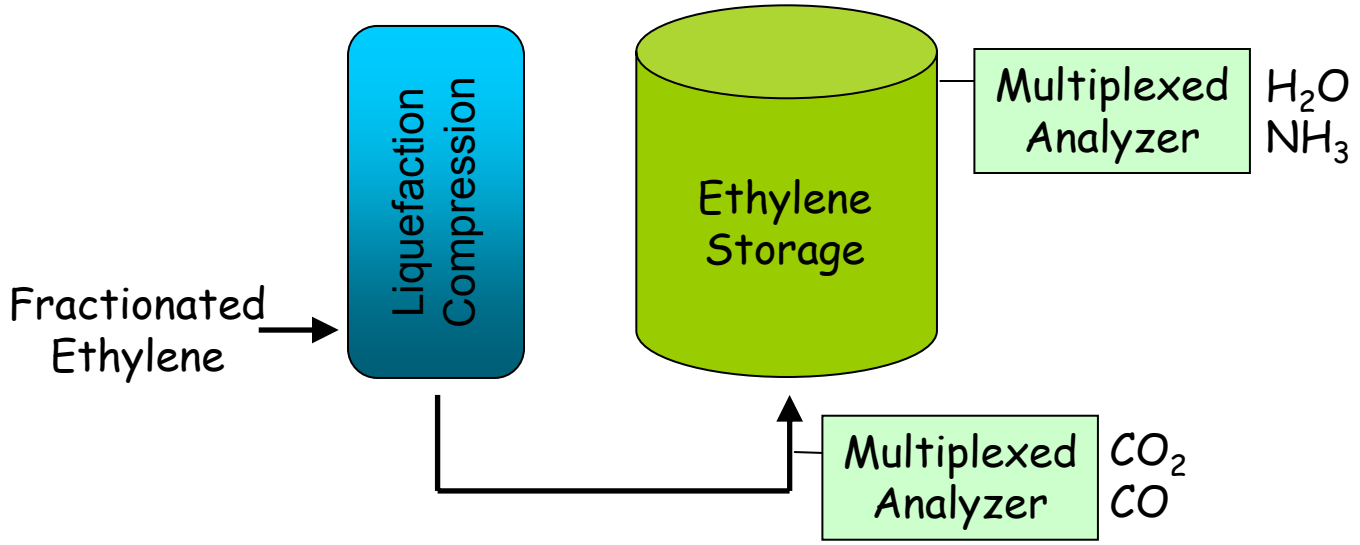
## Preliminary Studies – Other Contaminants




**LGR is assessing the feasibility of applying our Off-Axis ICOS technique to other contaminants ($C_2H_2$, $CO_2$, $NH_3$, CO) in ethylene and propylene.**

# Commercial Potential

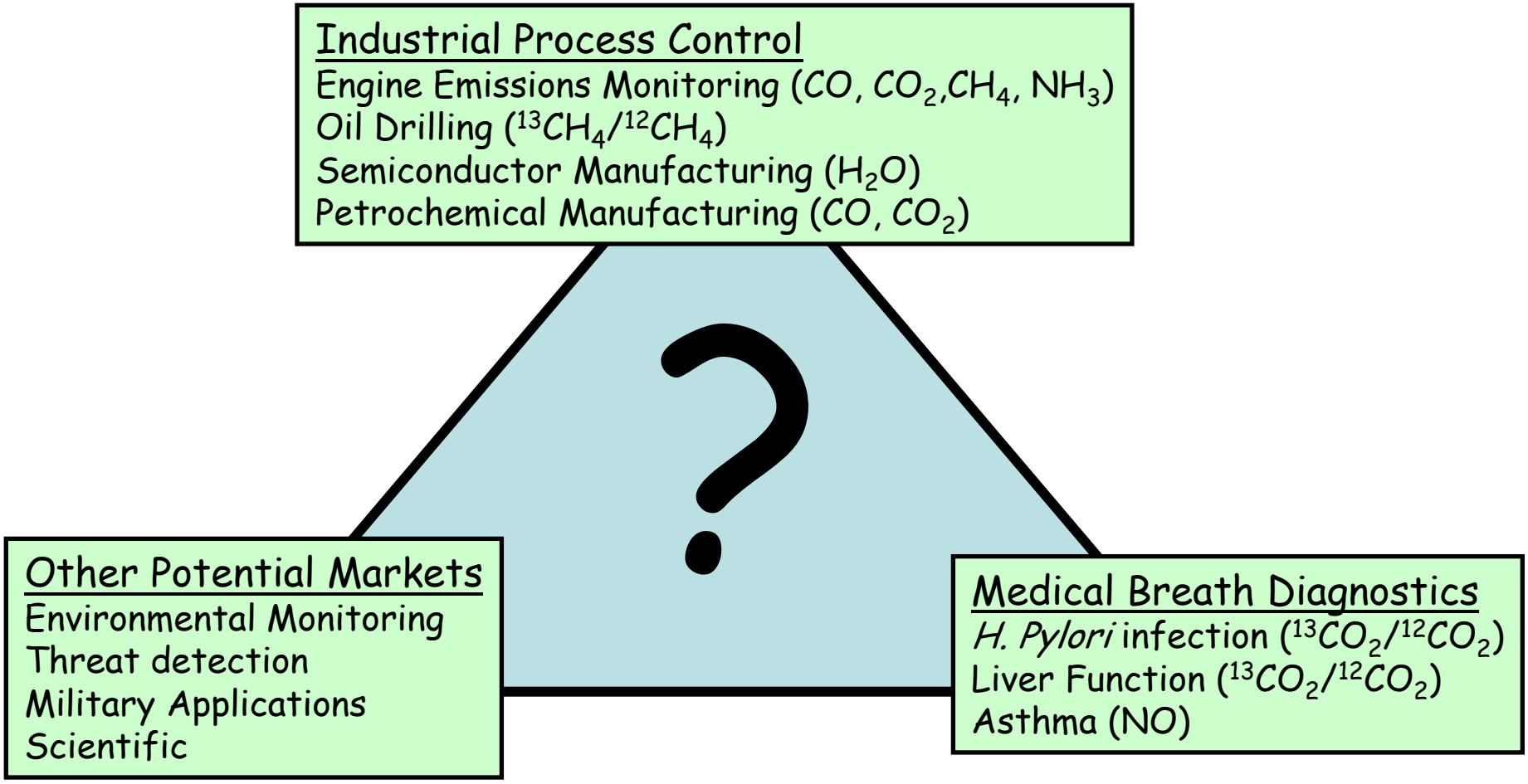
## Ethylene Process Control Analyzers




- 220 ethylene producing plants with 1-2 analysis points/plant = 200-400 analyzers
- Acetylene analyzer: ~$15k/analyzer + $4k/analyzer/year → $3-6M + $0.8-1.6M/year
- Multiplexed analyzer: ~$30k/analyzer + $4k/analyzer/year → $6-12M + $0.8-1.6M/year
- Due to recent ethylene market downturn, manufacturer's want high-return technologies
  - *OA ICOS analyzer will cost ~$100k/15 years, providing a savings of $200k/analyzer over GC*

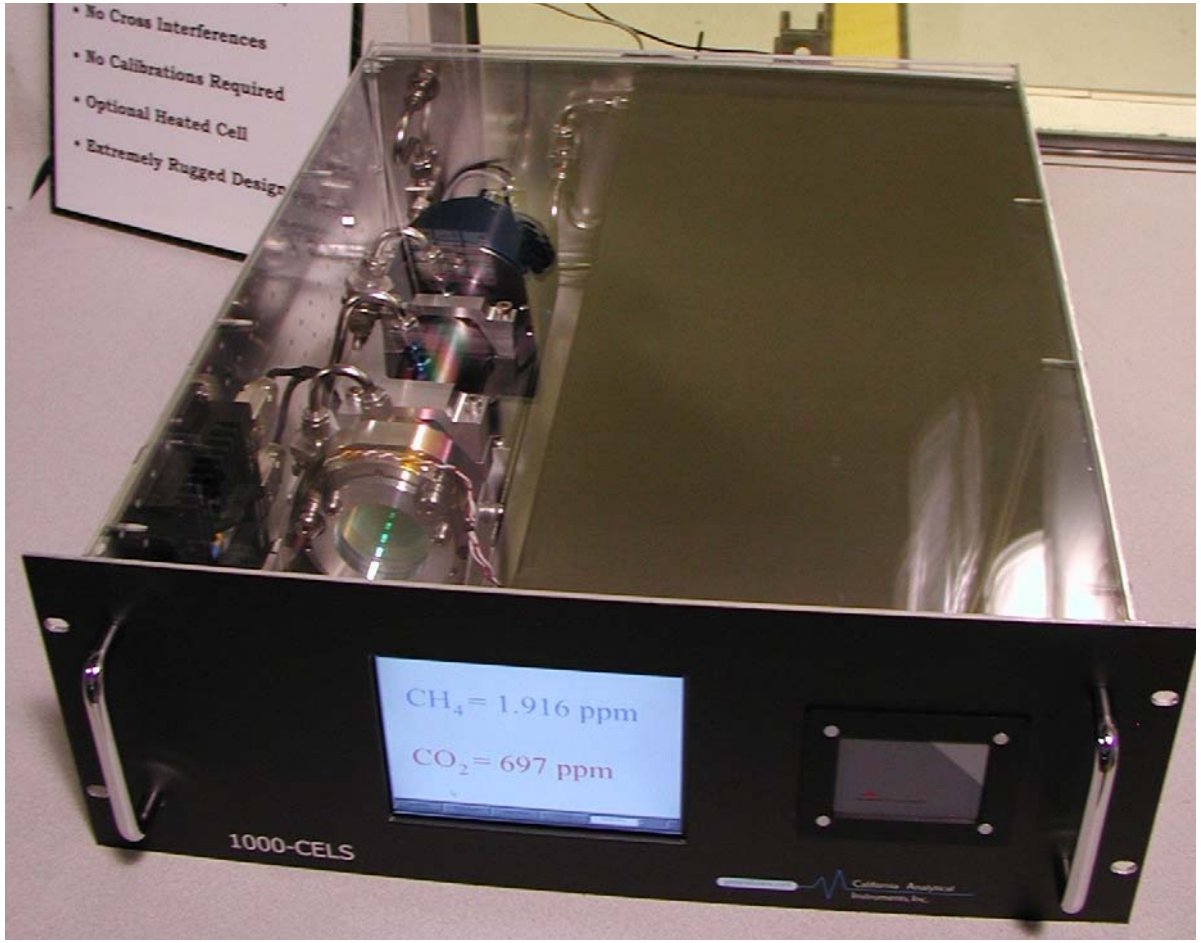
# Commercial Potential

## Other Markets



# Commercial Potential

## 1000-CELS




- 5 ppb < $CH_4$ < 100 ppm
- 50 ppb < $CO_2$ < 25%
- 10 Hz – modal analysis
- Automotive Applications
- Manufactured by LGR
- Distributed by CAI
- Tested by General Motors

**Gases**

| | |
|---|---|
| $CH_4$ | $C_2H_2$ |
| $CO$ | $CO_2$ |
| $H_2O$ | $HCl$ |
| $HF$ | $H_2S$ |
| $NH_3$ | $N_2O$ |
| $NO_2$ | $O_2$ |

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