# Industrial Applications of CES Instruments

**Applications, Advantages, Examples**

**Alejandro Farinas**

# Outline

Industrial applications of gas sensors

Advantages of CES in industrial applications

Design of an industrial sensor

Application examples

# Industrial Applications – Overview

- Specialty gas
- Manufacturing
  - Semiconductor fabrication
  - LEDs
  - Aerospace
  - Fuel cells
  - Purifier/catalyst development
  - Pharmaceutical
- Industrial emissions
  - Continuous emissions monitoring (CEM)
  - Process control

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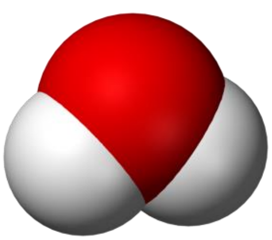
# Analytes and Matrices

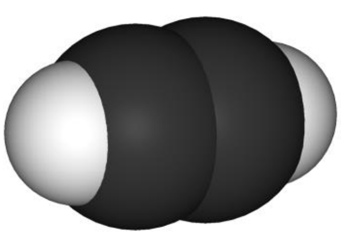
## Available analytes

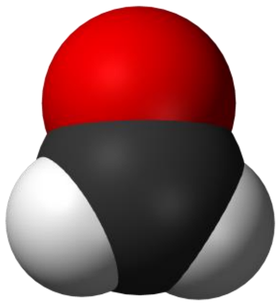
- $CH_4$
- $H_2O$
- $H_2CO$
- $CO_2$
- $NH_3$
- $H_2O_2$
- CO
- HF
- $N_2O$
- $C_2H_2$
- HCl
- $H_2S$

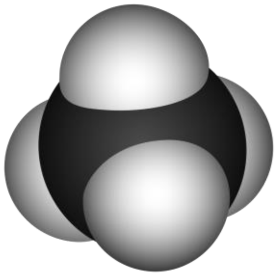
## Matrices

- Inerts: $N_2$, He, Ar, $CO_2$, air
- Mixtures
- Corrosives
- Reactive gases









# Commercialized Cavity-Enhanced Technology

PICARRO — Cavity ring-down spectroscopy

LGR — Off-axis integrated cavity output spectroscopy

TigerOptics — Cavity ring-down spectroscopy

ap2e — Optical feedback cavity enhanced absorption spectroscopy

# Advantages of Cavity Enhanced Techniques

- Low detection limit
- Linear
- Selective
- Small sample volume
- Low drift
  - fewer calibrations
- Robust
  - reliable
  - transportable
- Easy to Use
  - small footprint
  - remote operation
- Low cost of ownership
  - no consumables
  - minimal gas usage

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# Displacement of Incumbent Technologies

| Established/Potential Applications | Displaced technology |
|---|---|
| Continuous emissions monitoring (CEM) | Fourier Transform Infrared, non-dispersive infrared, gas filter correlation<br><br>Proven technique for HCl CEM – validated by EPA and Electric Power Research Institute (EPRI) |
| Fuel cell hydrogen purity analysis | Gas chromatography<br><br>ASTM D7941 / D7941M – 14 - Standard Test Method for Hydrogen Purity Analysis Using a Continuous Wave Cavity Ring-Down Spectroscopy Analyzer |
| Airborne molecular contamination cleanroom monitoring | Ion mobility spectrometry |
| Industrial process control | Gas chromatography, chemiluminescence, fluorescence |
| Semiconductor manufacturing | Electrochemical, chilled mirror |
| Air quality monitoring | Chemliuminescence ($NO_x$), fluorescence ($SO_2$), ozone (UV photometer) |
| Food origin | Mass spectrometry (isotopic ratio analysis) |

# Technology Comparison: Trace Gas Analysis

| | Measures a Few Compounds | Measures Multiple Compounds |
|---|---|---|
| **Higher Performance** | TDL<br>• Low initial cost<br>• Higher cost of ownership<br>• Continuous measurements<br>CES<br>• High initial cost<br>• Low cost of ownership<br>• Continuous measurements | Chromatography<br>• High initial cost<br>• High cost of ownership<br>• Discrete measurements |
| **Lower Performance** | NDIR<br>• Low initial cost<br>• Higher cost of ownership<br>• Continuous measurements<br>Electrochemical<br>• Very low initial cost<br>• Continuous measurements | FT-IR<br>• High initial cost<br>• Lower cost of ownership<br>• Continuous measurements |
| | Typically Field Deployable | Typically Laboratory Based |

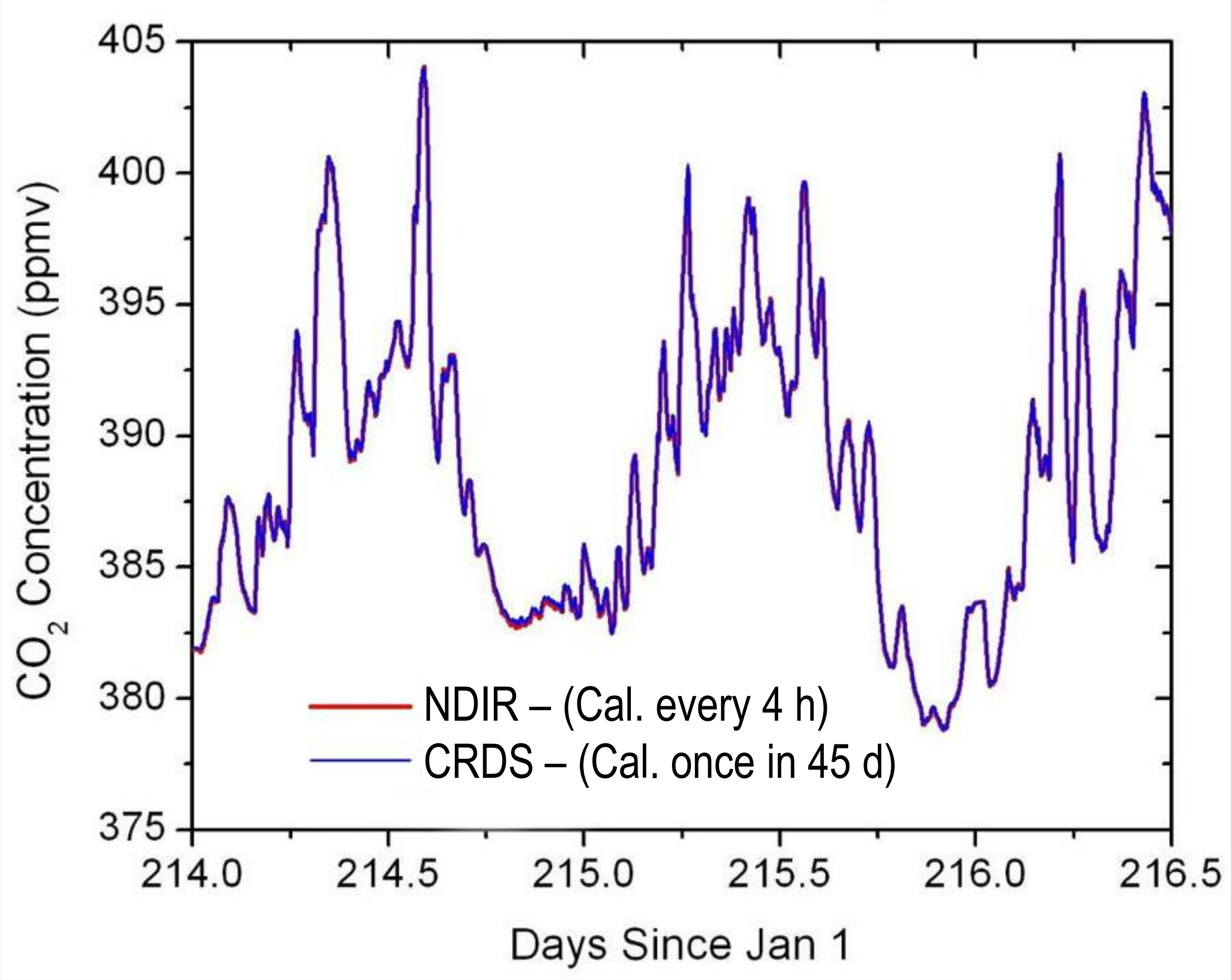
# Technology Comparison: Isotope Analysis

- IRMS
  - (+) High performance
  - (+) Flexibility
    - many compounds in a single instrument
  - (-) Selectivity
    - many interferences complicate sample prep and analysis
  - (-) Expensive
    - challenging to use and to maintain
- CES
  - (o) Good performance
  - (-) Flexibility
    - a given spectral region accesses a small subset of compounds
  - (+) Selectivity
    - identical mass isotopologues are easily distinguished (little or no sample prep)
  - (+) Inexpensive
    - easy to use and to maintain

Courtesy of Prof. S. Benson (Stanford U.)

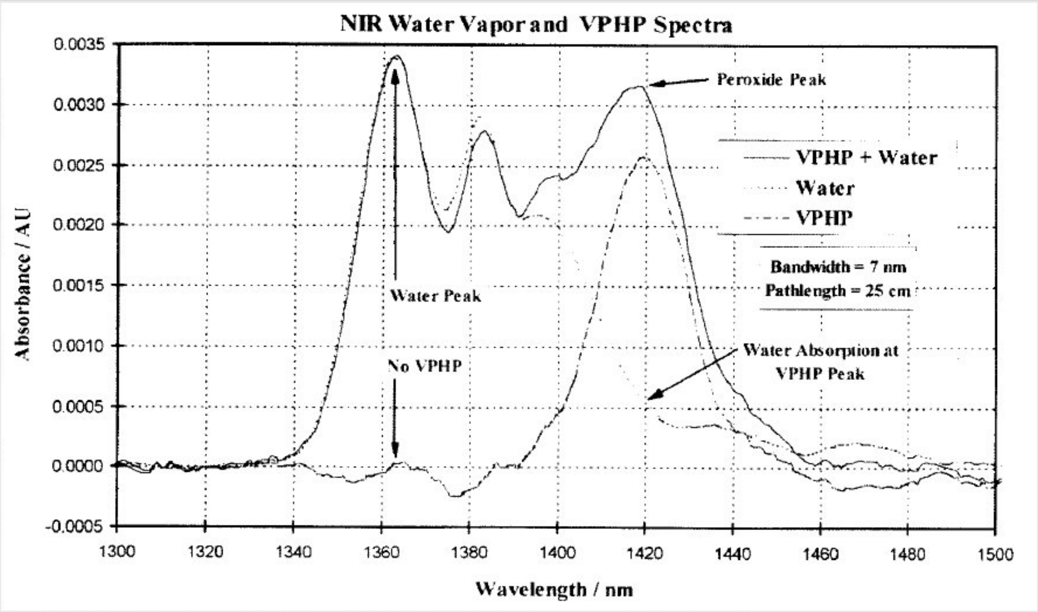
# Calibration Interval

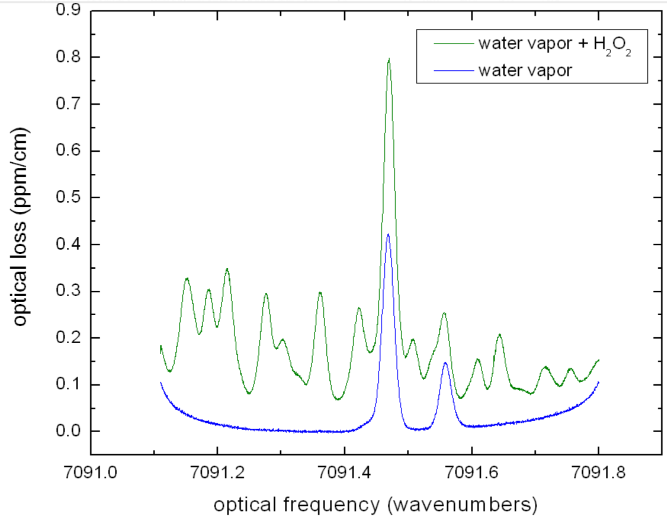
- Require frequent calibration
  - IRMS
  - GC
  - FT-IR
  - TDL
  - NDIR
  - Electrochemical
- Require infrequent calibration
  - CES (especially CRDS)



# Selectivity

- Less selective
  - IRMS
  - FT-IR
  - NDIR
- More selective
  - GC
  - CES
  - TDL
  - Electrochemical




(top) Pharmaceutical Engineering **18**, May/June 1998

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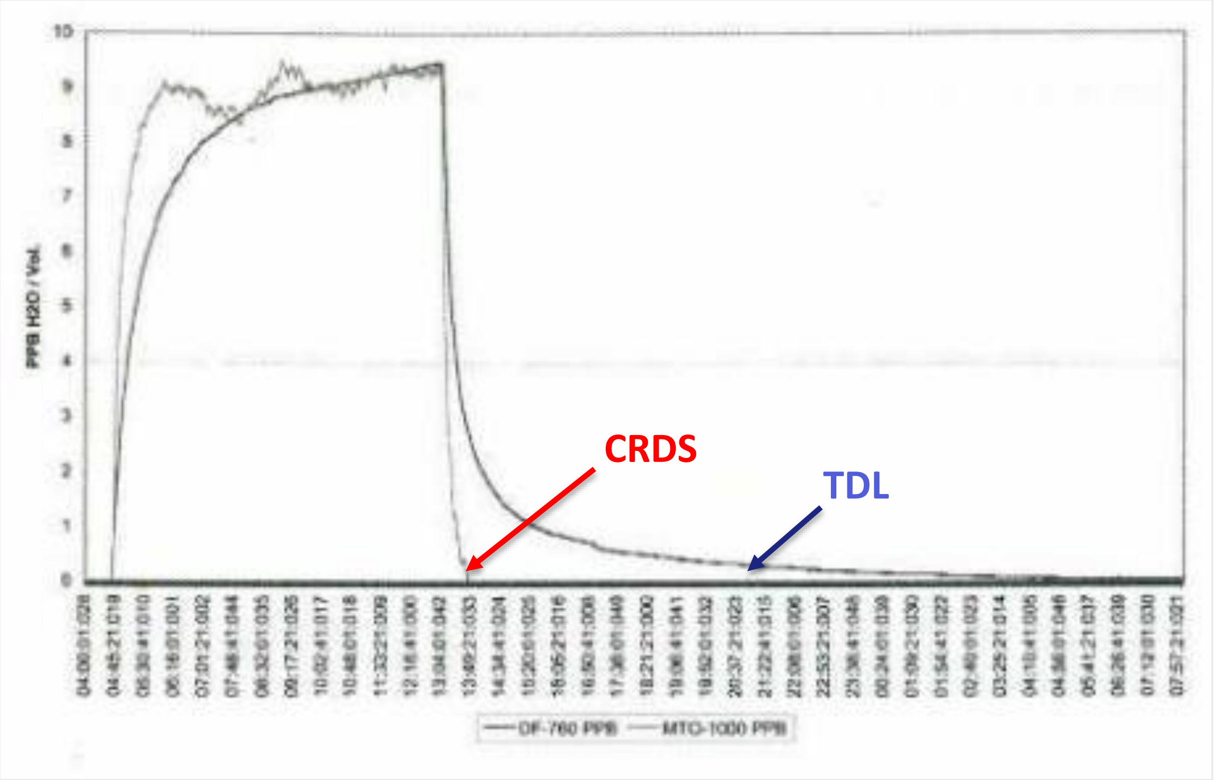
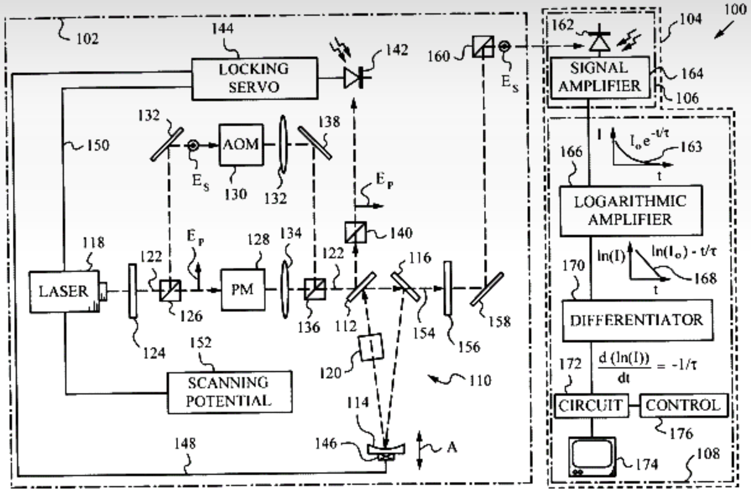
# Response Time

- Slow response
  - FT-IR
  - TDL
  - NDIR
  - Electrochemical
- Fast response
  - CES




"Qualitative Comparison of Cavity Ring-Down vs. Direct Measurement Absorption Spectroscopy for Determining ppb Moisture Levels in UHP Gases" Gases & Technology, May/June 2004

# Commercialization Challenges



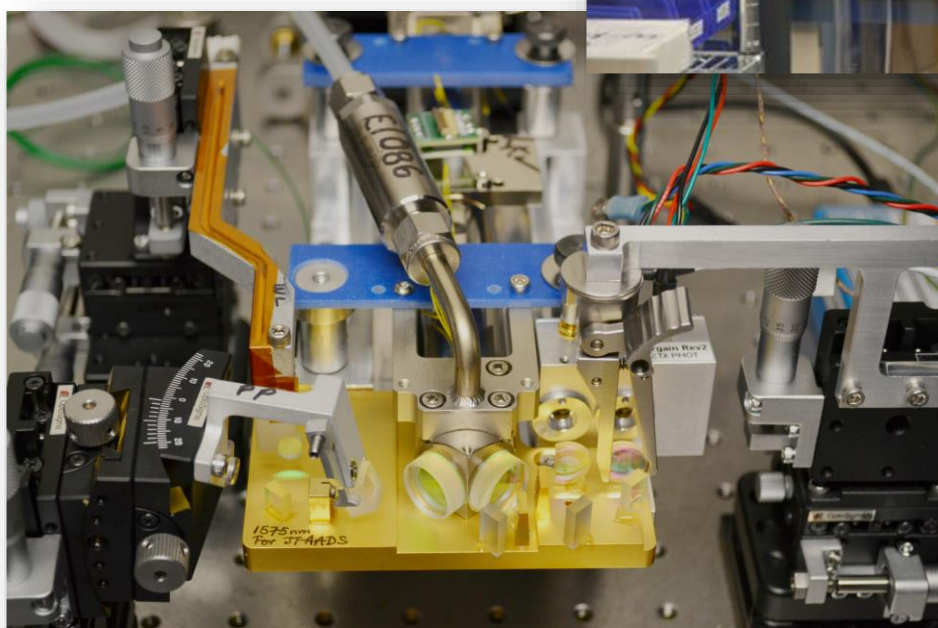

- Technology
  - Superior technology is often necessary at a startup but not always sufficient for success

- Flexible platform
  - The commercially successful application of a given technology is rarely known at the time of design

More in Hobbs, *Building Electro-Optical Systems: Making It All Work* , ch. 11 and 19 (Wiley, New York)

# Commercialization Challenges

- Design for manufacturability
  - Product cost structure is mostly “baked in” at design
    - Labor
    - Tooling, process
    - Scrap, yield



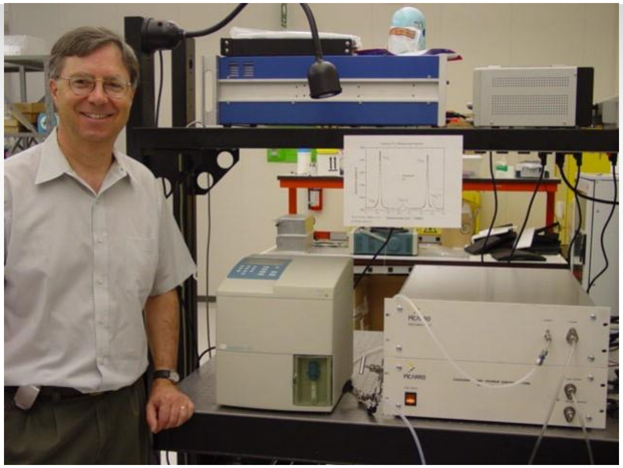
# Commercialization Challenges

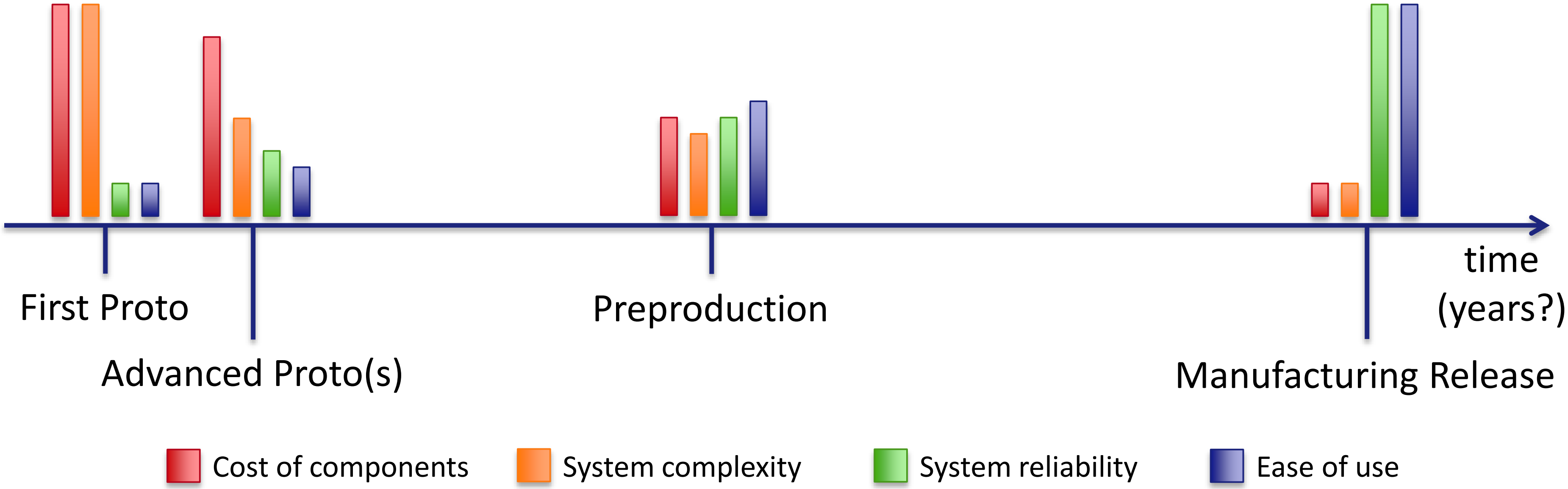
- Reliability
  - Product lifetime
  - Surviving shipping is surprisingly difficult



- Test plan
- End of Life
  - Inventory
  - Support/Repair

# Product Development



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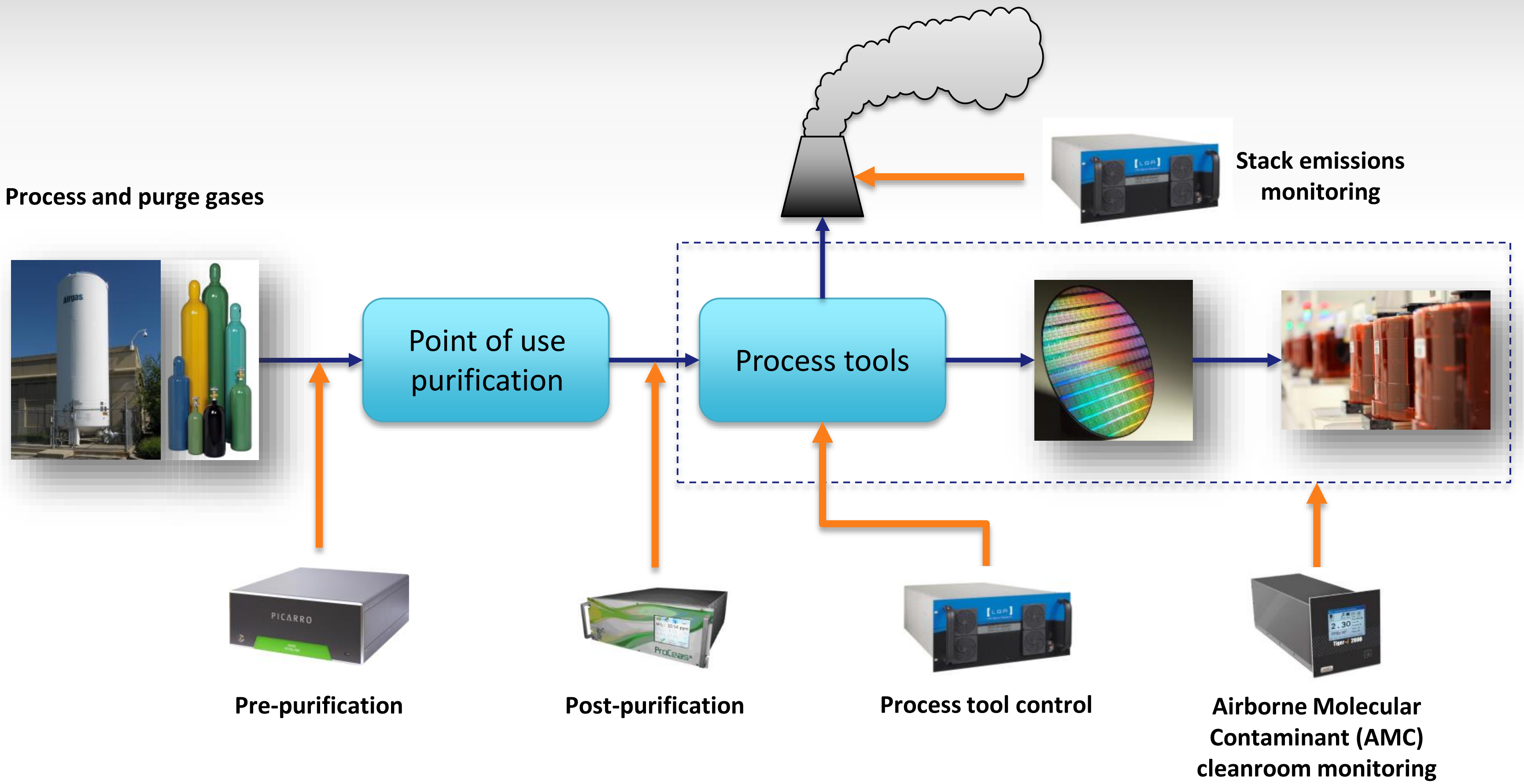
# Market Penetration




- Time to adoption can be very long
  - A satisfactory solution is probably already in place
  - Introducing new sensors means changing the manufacturing process

# Application: Drilling Ice Cores in the Arctic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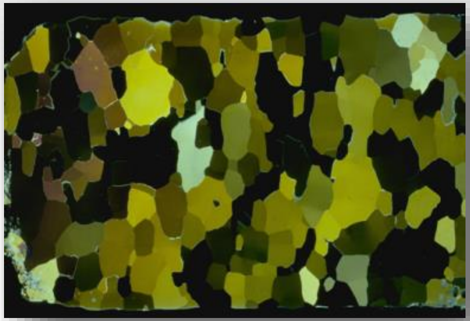
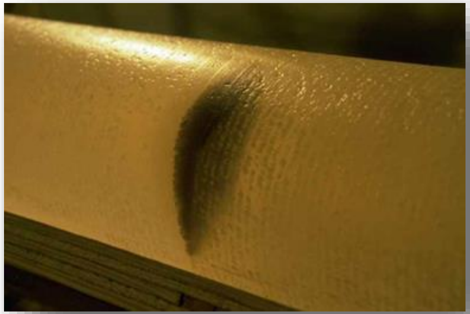
# Climate Archives in Ice Cores

Precipitation (water isotopes)



Things trapped in the Ice



Air bubbles

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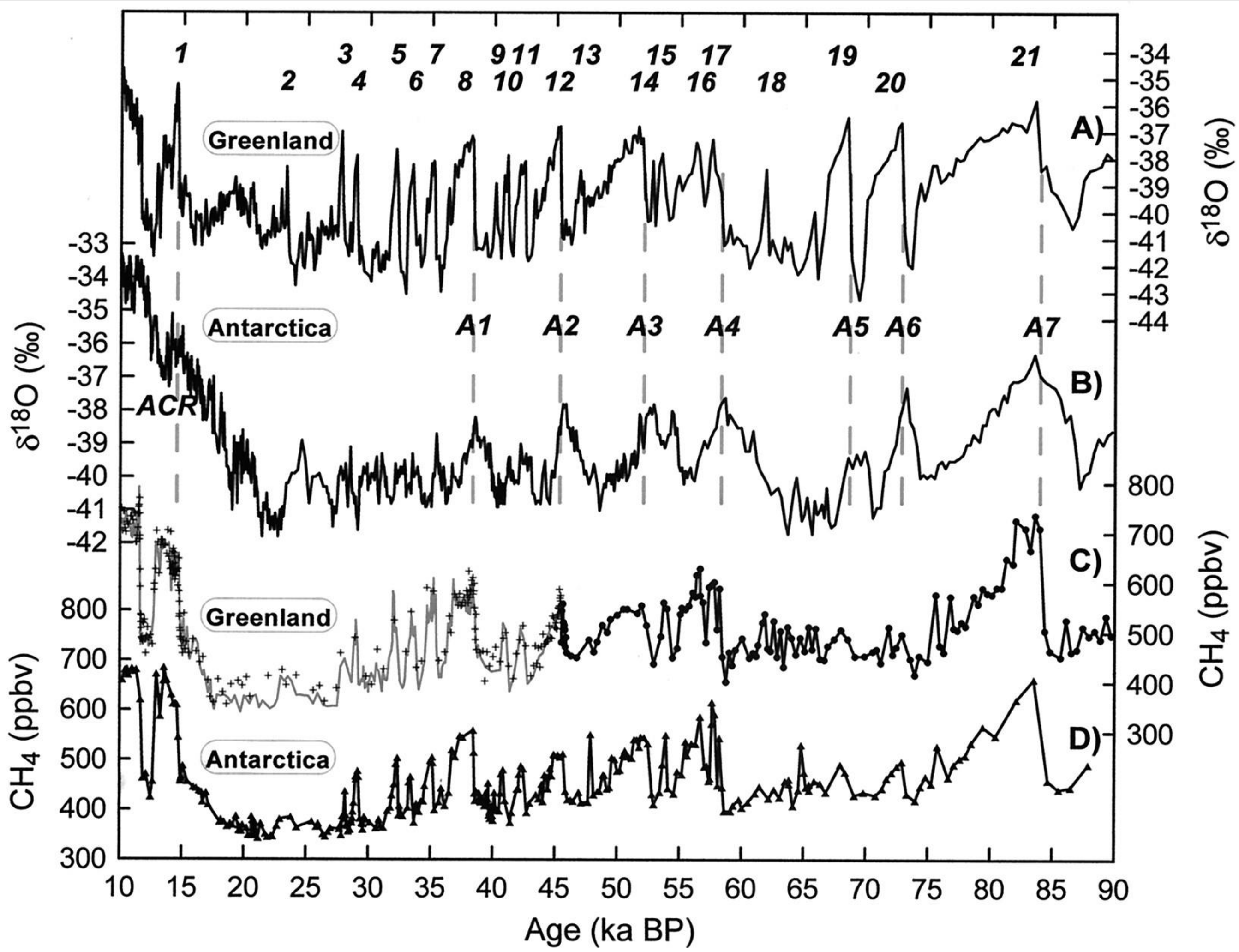
# Isotopes Provide Historical Temperature Information




See: Blunier and Brook, *Science*, Volume 291, 109-112, 5 January 2001

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# Commuting to a Glacier


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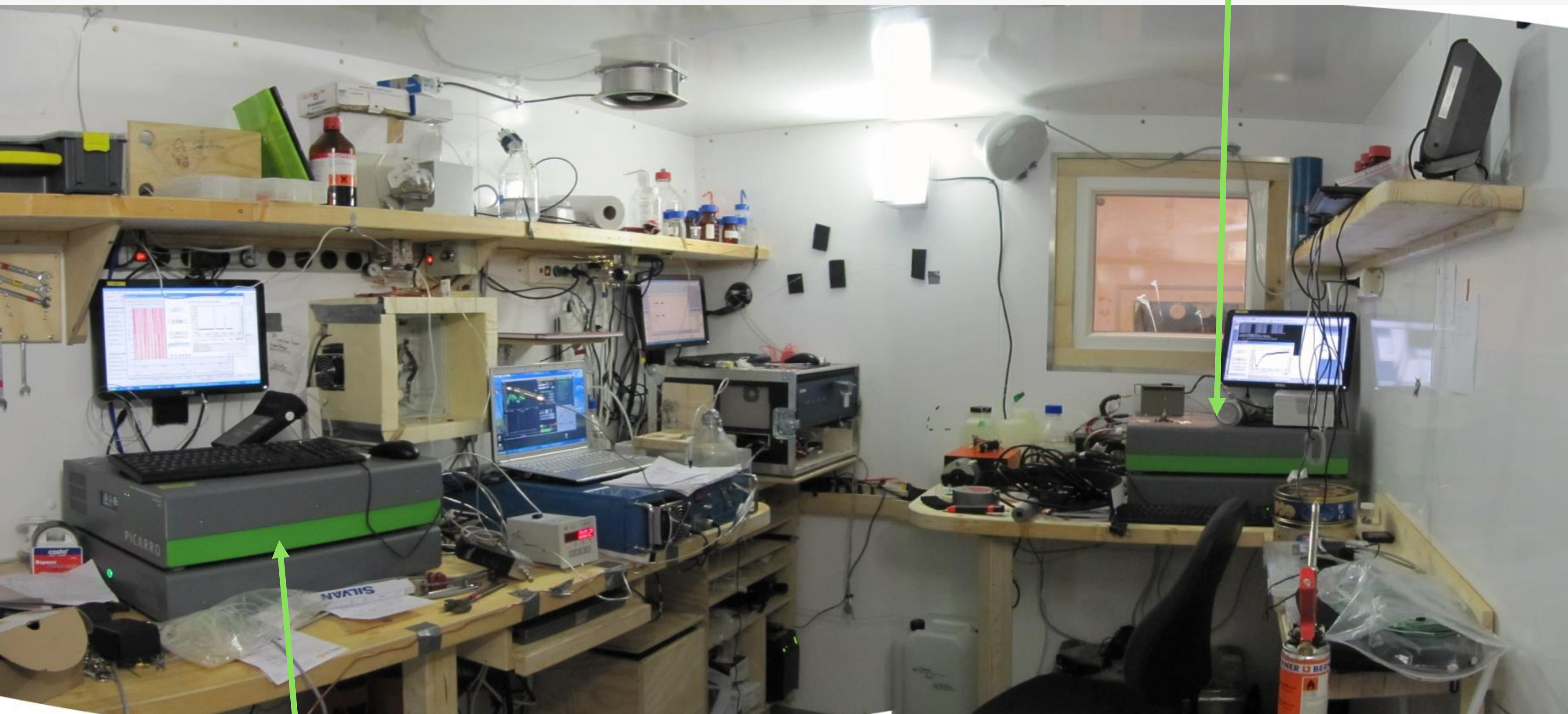
# CES Instruments in Greenland

$H_2O$ isotope measurements

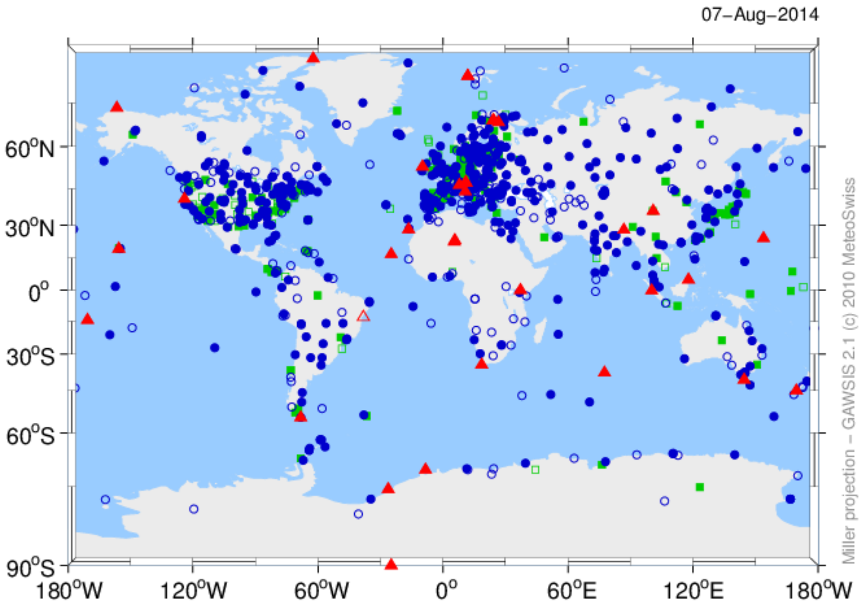



On line $CH_4$ measurements

(Not shown, prototype OF-CEAS $CH_4/N_2O$ instrument)

# Application: GHG Networks

- WMO's Global Atmospheric Watch (GAW) program provides reliable scientific data and information on the chemical composition of the atmosphere and helps to improve our understanding of interactions between the atmosphere, the oceans and the biosphere.
- Combines traditional flask sampling (e.g., NOAA's ESRL cooperative air sampling network) with in-situ high precision tower measurements

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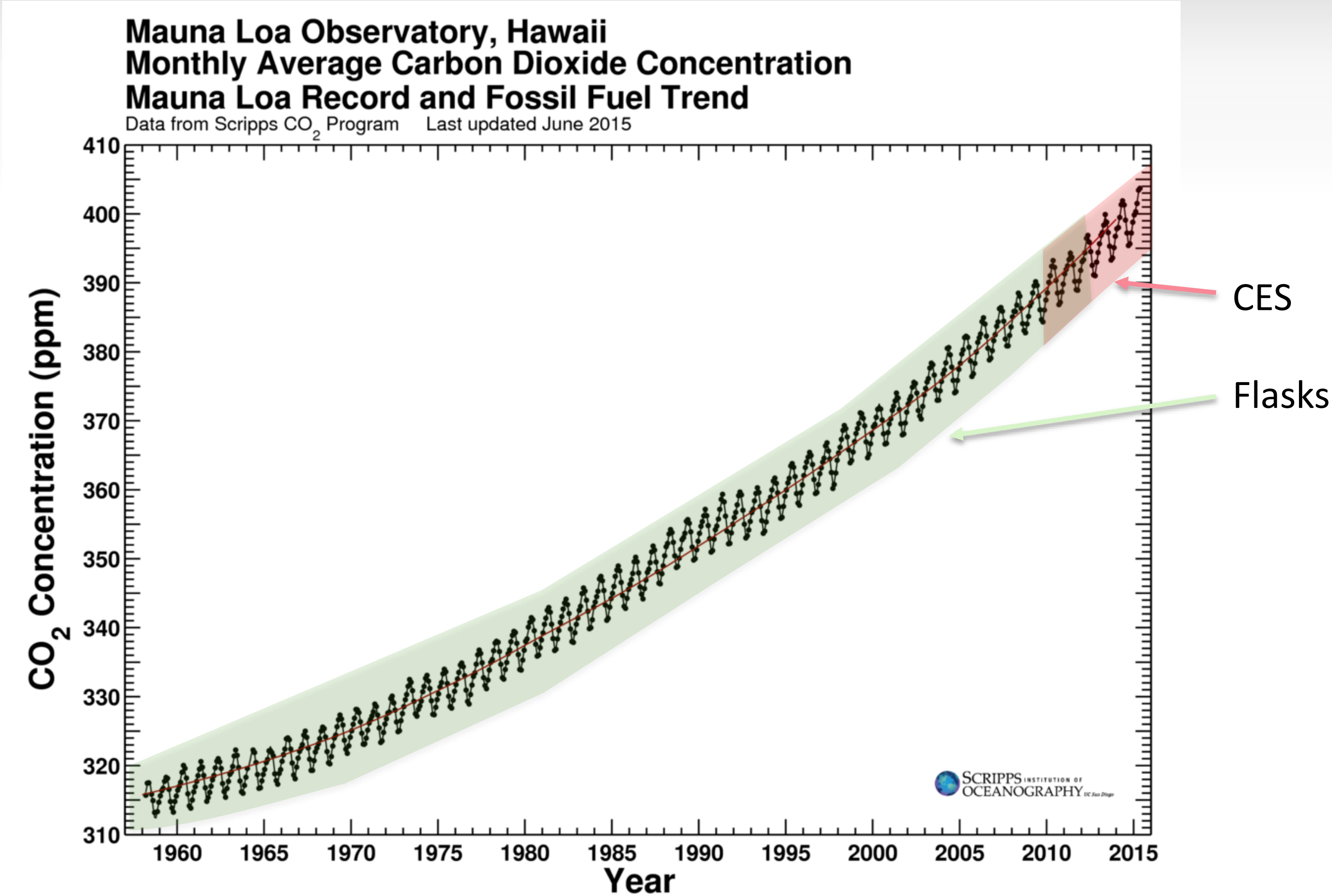
# Flask Sampling

http://instaar.colorado.edu/arl/Global_VOC.html

# The Mauna Loa $CO_2$ Record




http://scrippsco2.ucsd.edu/graphics_gallery/mauna_loa_record

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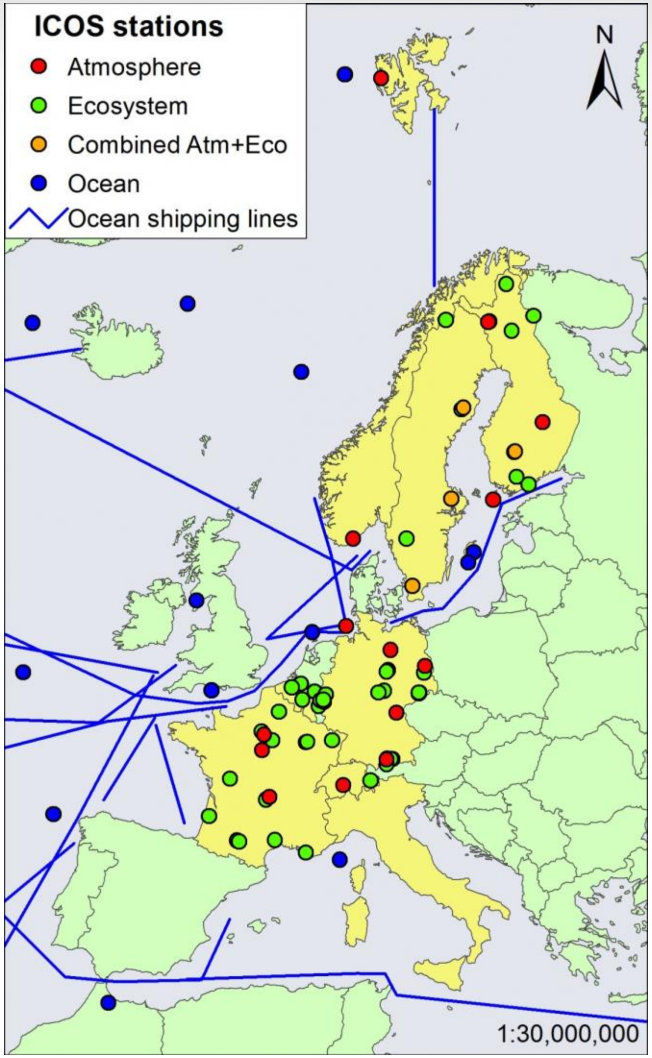
# Regional Networks

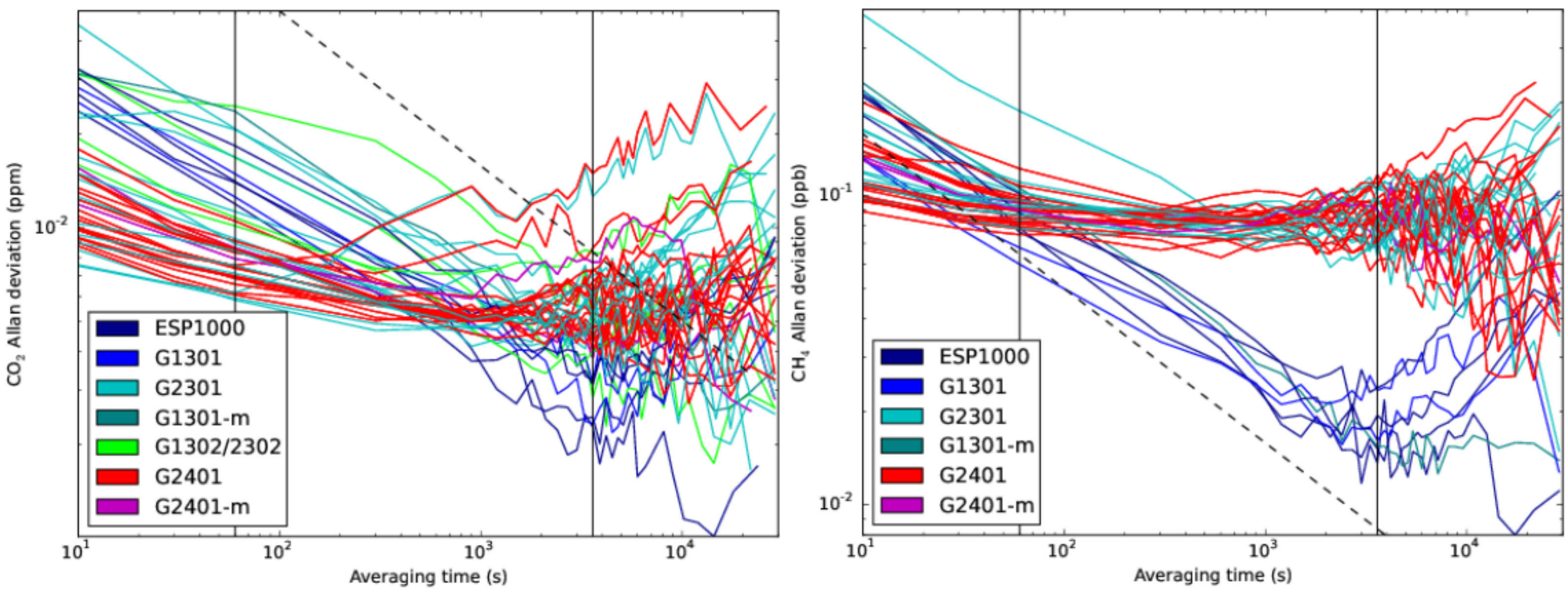
- "Measurements of greenhouse gases in Europe have suffered from heterogeneity, discontinuity and lack of sustainability in the long term"
- "Providing standardized and automated high precision measurements is therefore a key focus of ICOS"
- "Comparability of data is obtained through the use of measurement protocols and standardized instrumentation"




https://www.icos-ri.eu/

# Intercomparability

- “Instruments in the field need to be stable and precise and thus require infrequent calibrations and a low consumption of consumables.”
- “For about ten years, cavity ring-down spectroscopy (CRDS) analyzers have been available that meet these stringent requirements for precision and stability.”
- “Newer models generally perform better than older models, especially in terms of reproducibility between instruments.”

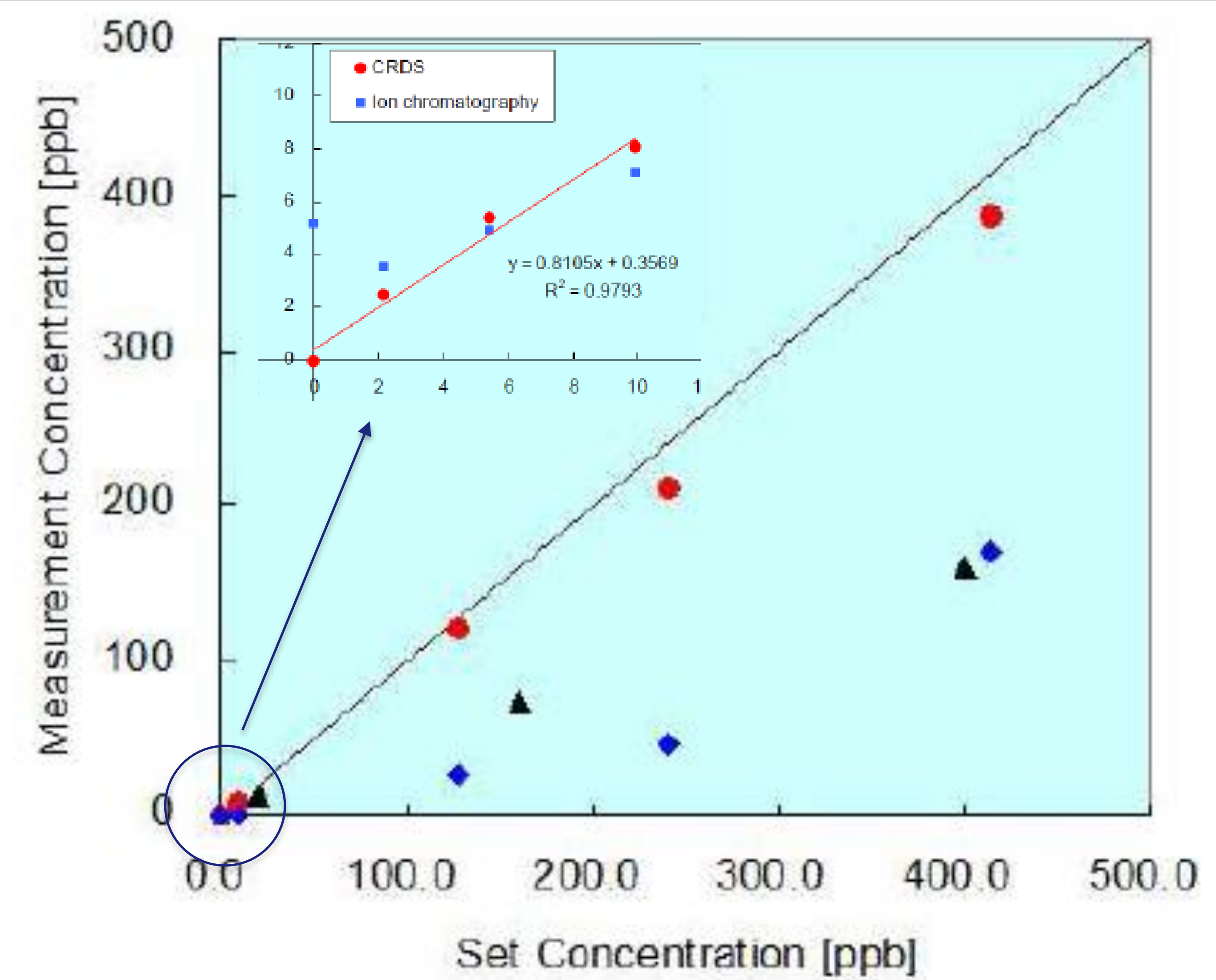



Yvor Kwak, *et al.*, Atmos. Meas. Tech. Discuss., 8, 4219-4272 (2015)

# Application: Airborne Molecular Contamination

- Product yield adversely affected by presence of airborne molecular contaminants (AMC)
- AMC critical during deposition, etching, and cleaning operations
- Key species
  - HF, $NH_3$, HCl
  - Key performance criteria
    - LDL – sub-ppb
    - Speed of response
    - Stability
    - Ease of use
    - Cost of ownership
- Incumbent technologies – ion mobility spectrometry, pulsed fluorescence

# Comparison with Ion Chromatography



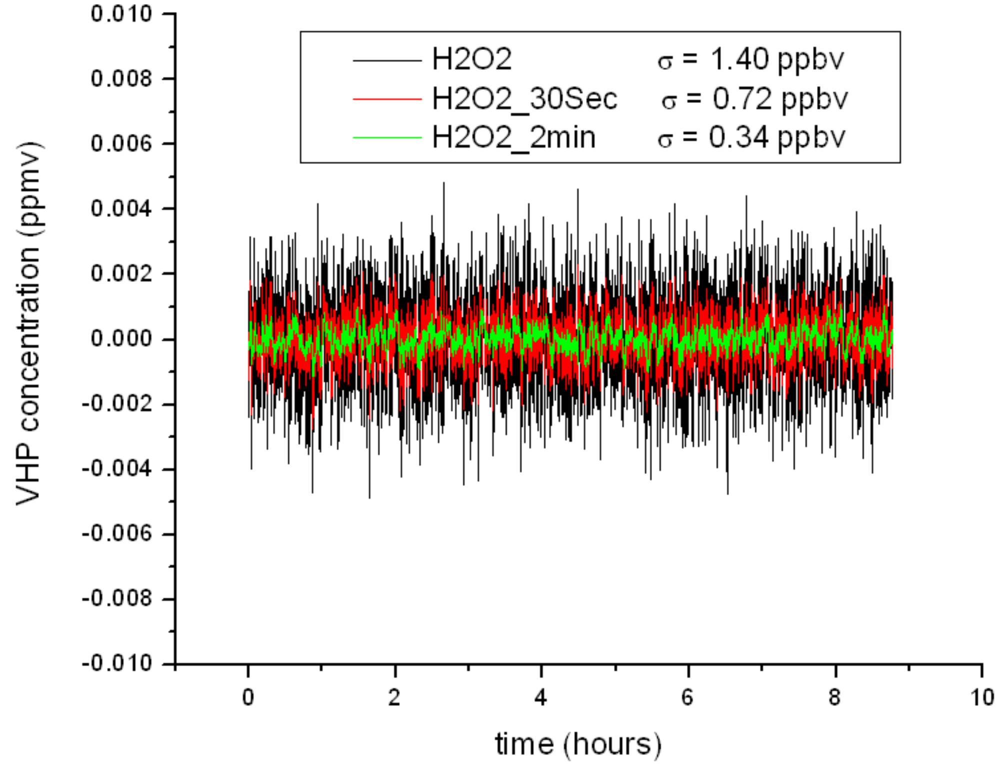

Nishimura et. al. "Real-time trace ambient ammonia monitor for haze prevention", Proc. of SPIE Vol. 6607, 66071Y, (2007)

# Application: Bio-decontamination

- Used in pharmaceutical industry
  - Monitor VHP (Vapor Hydrogen Peroxide) concentration during bio-decontamination
  - Confirm removal of $H_2O_2$ during aeration, some biological materials show sensitivity to in the ppb range

# Detection Limit

CES




Typical electrochemical sensor

Resolution: 100 ppb

Response time: 60 s

(Complicated calibration procedure)


(right) http://www.draeger.com/sites/assets/PublishingImages/Products/X-am_5100/US/x-am-5100-pi-9041413-us.pdf

# Optimizing Throughput

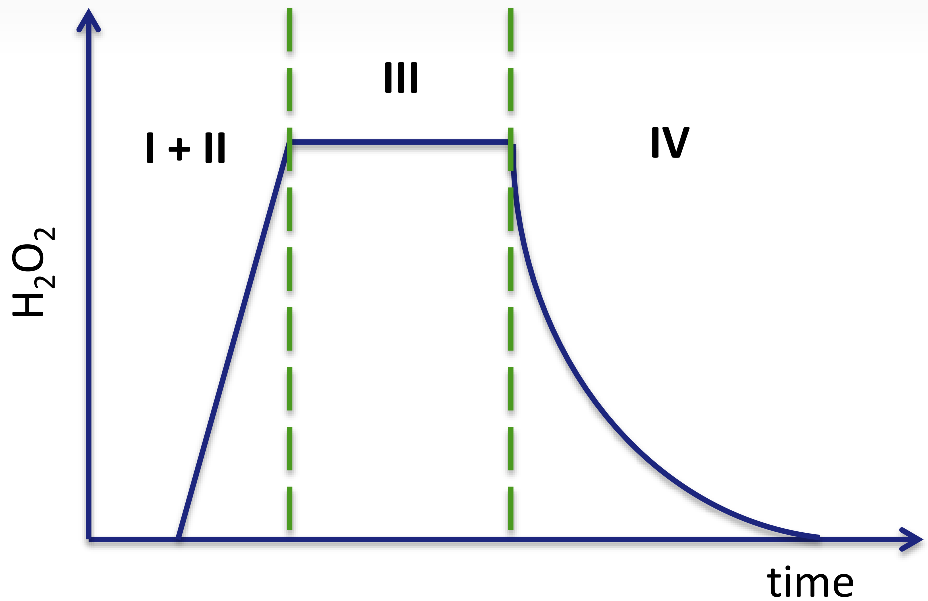


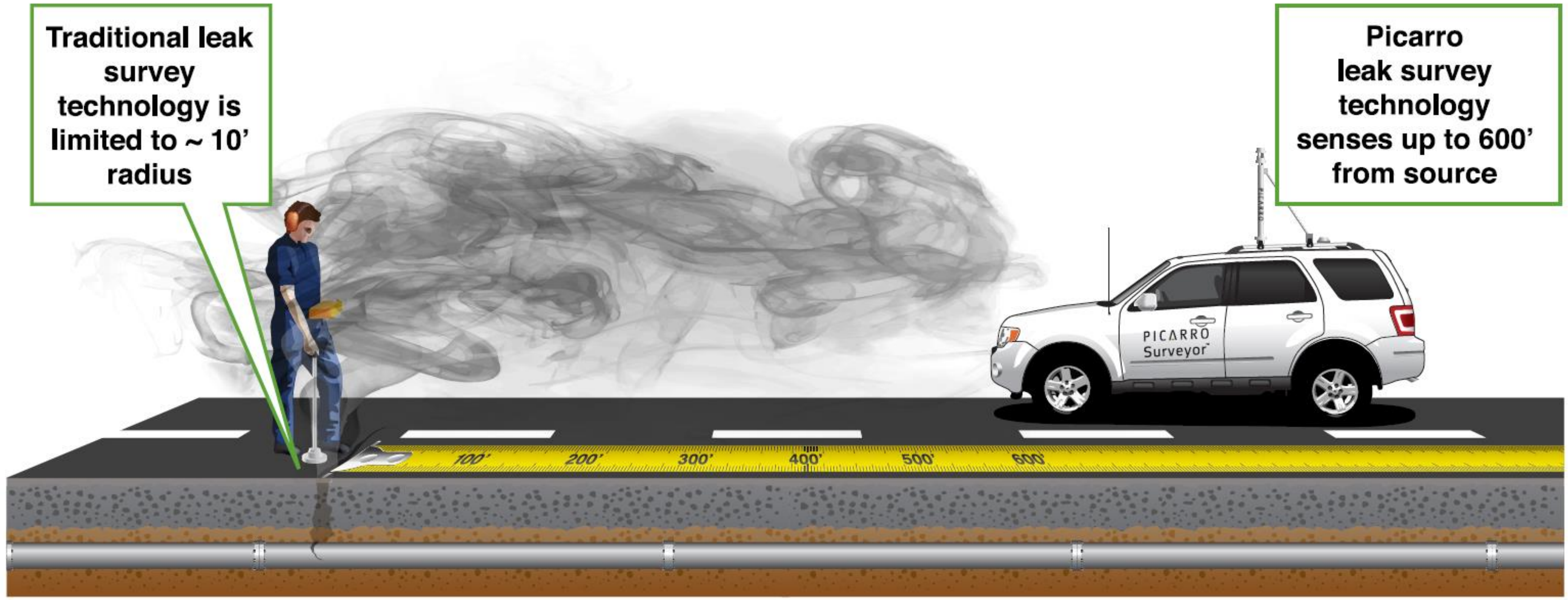

**Table I: Settings used for each cycle during performance qualification.**

| | |
|---|---|
| **Steris VHP 1000ED biodecontamination system** | |
| *Airflow 20 SCFM* | |
| Phase I: Dehumidification | 15 min and RH <4.6 mg/L |
| Phase II: Conditioning | 2 min at 5.6 g/min |
| Phase III: Decontamination | 34 min at 3.5 g/min |
| Phase IV: Aeration | 2 to 5 hours |
| **Bioquell Clarus "C" $H_2O_2$ gas generator** | |
| *Airflow 500 L/min (~18 SCFM)* | |
| Phase I: Conditioning | 10 min and 40% RH |
| Phase II: Ramp gassing | 15 min at 1.5 g/min |
| Phase III: Dwell gassing | 12 min at 1.1 g/min |
| Phase IV: Aeration | 2.5 to 3 h |

The cycle times listed above are the full cycle times. During the PQ, the VHP 1000ED's Phase III and the Clarus's Phases II and III were run at three quarters of the times listed above.

(left) Adapted Robert Bosch GmbH (2007)
(right) http://images.alfresco.advanstar.com/alfresco_images/pharma/2014/08/22/16520042-9a7c-4b5c-b767-483c6a68bb63/article-132395.pdf

# Application: Gas Leak Detection

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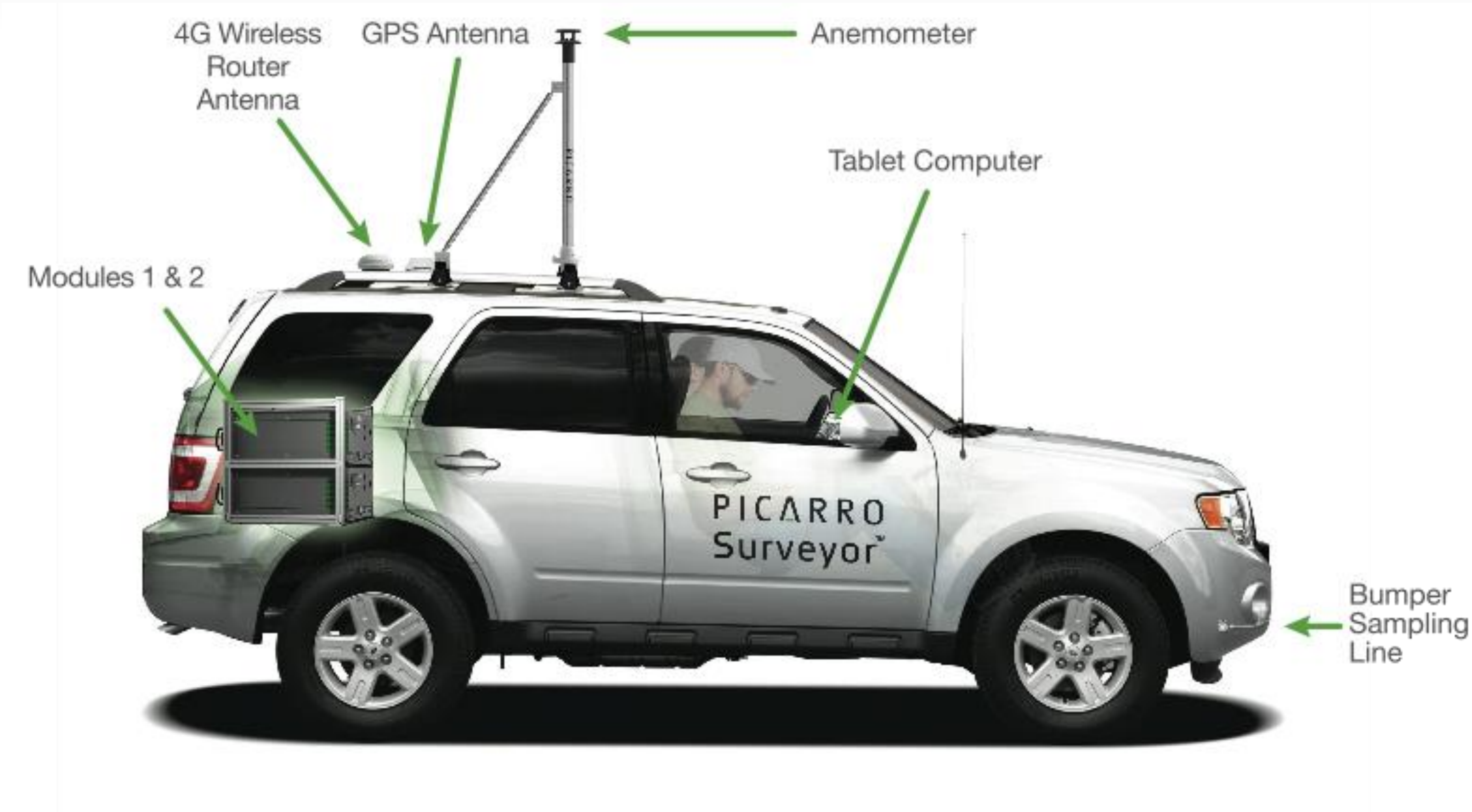
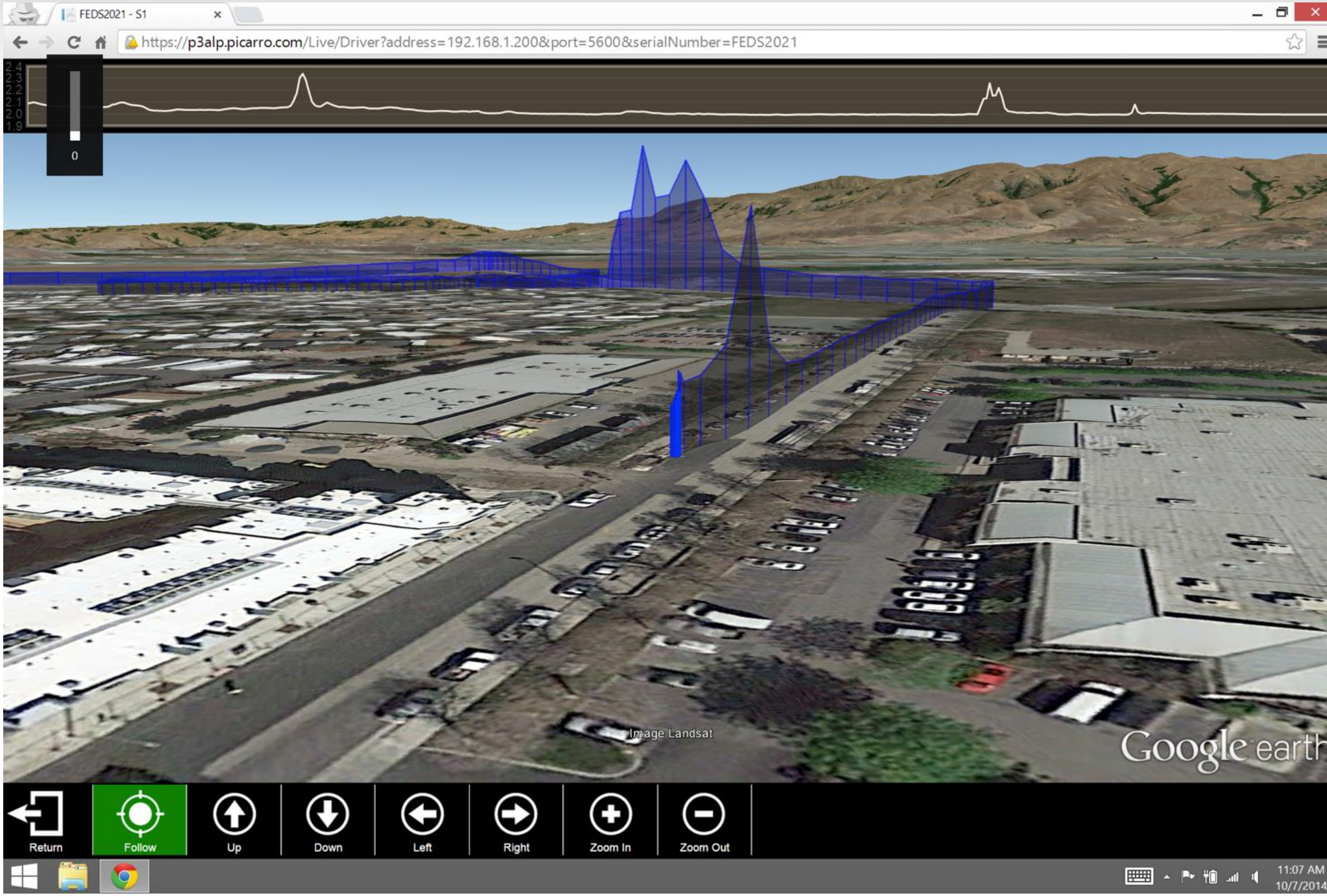
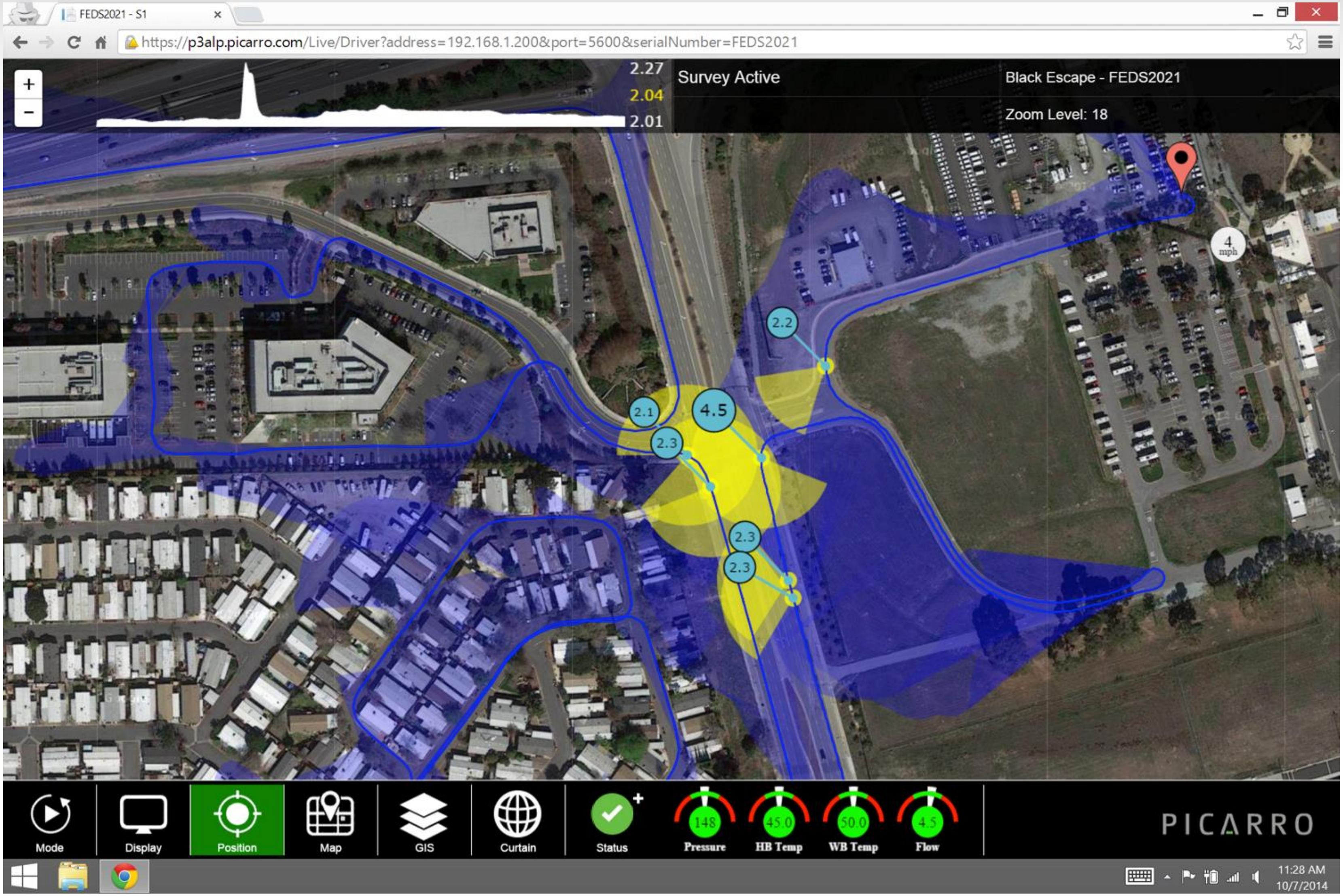
# Mobile Methane Detection



# Methane Concentration Measurement



# Sophisticated User Interface

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# Summary

- Ease of use and reliability are as important as sensitivity and drift

- Cost calculations must take into account the cost of operation, calibration, training, etc.

- Displacing an established technology is very difficult

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