# Highly Selective and Stable Multivariable Gas Sensors

## for Enhanced Robustness and Reliability of SOFC Operation

NETL Contract FE0027918


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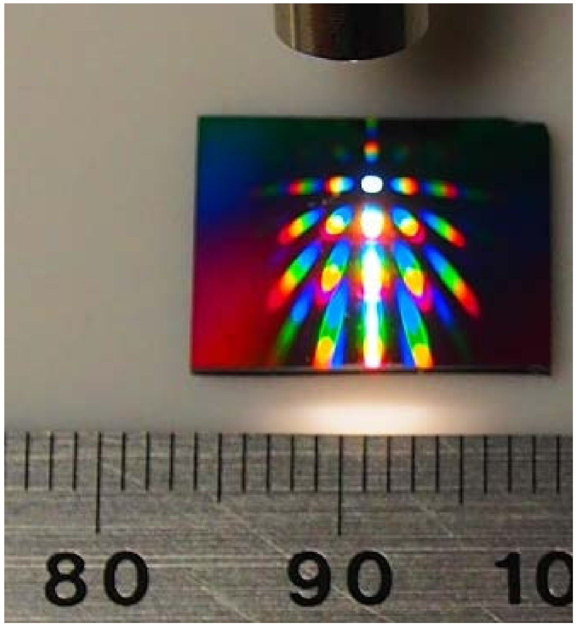
19th Annual SOFC Project Review Meeting,
Washington, D.C., June 13-15, 2018


# Project overview

## Project strategy:

Develop in-line gas sensor for real-time SOFC diagnostics and enhancement of operation reliability

## Project approach:

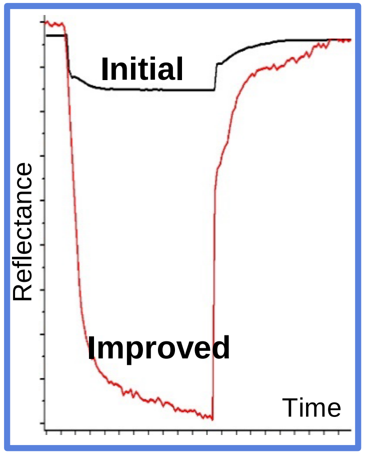
Implement bio-inspired multivariable gas sensors for multi-gas quantitation at high temperatures
Perform laboratory optimization followed by field validation

## Phase 1 outcomes:

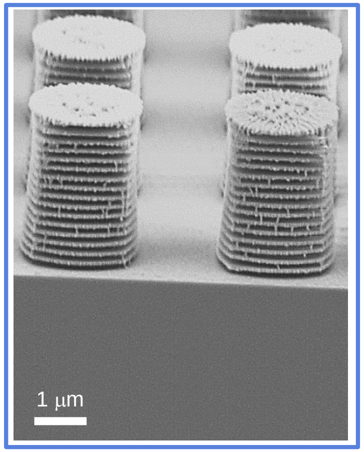
Fundamental understanding of performance and development of design rules of multivariable gas sensors at high temperatures

## This year top FIVE accomplishments

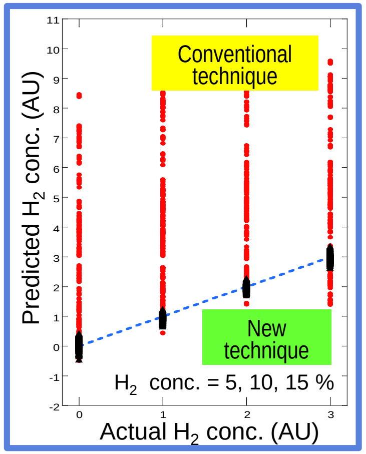
### Sensitivity control



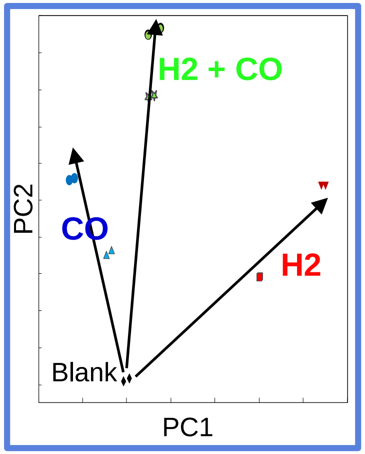

### Selectivity control



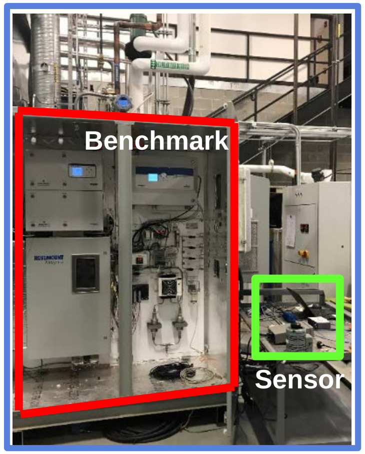

### Sensor stability




### Detection of gas mixtures




### Initial field validation



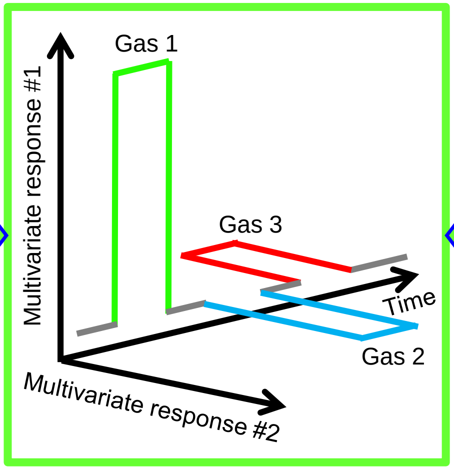
# Unmet need for real-time monitoring of $H_2$ and CO gases

**Real-time knowledge of $H_2$/CO ratio (3:1–2:1) of anode tail gases:**

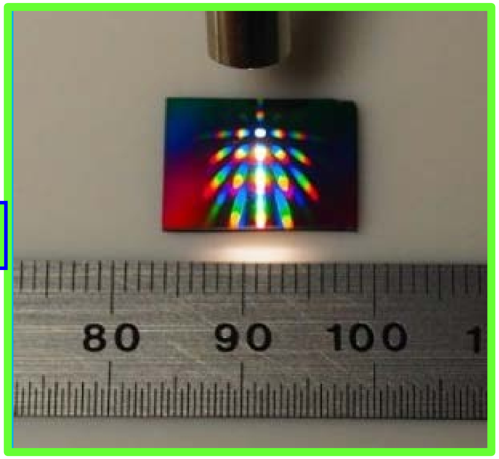
- will allow control of efficiency of reforming process in the SOFC system
- will deliver a lower operating cost for SOFC customers

**Status quo:**
Mature traditional detector concepts


**Performance need:**
Multi-gas discrimination

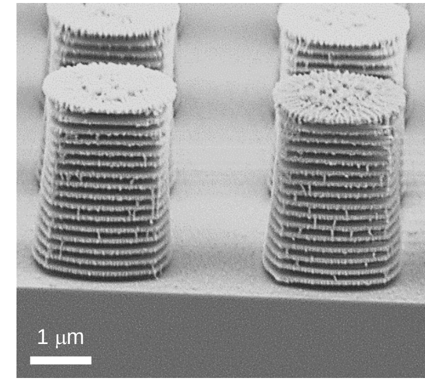



**Our approach:**
Multivariable photonic gas sensors




In-line gas detection is not straightforward

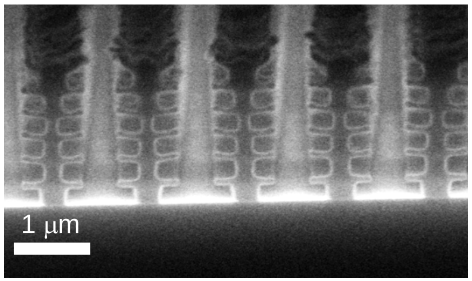
# Learning from Nature

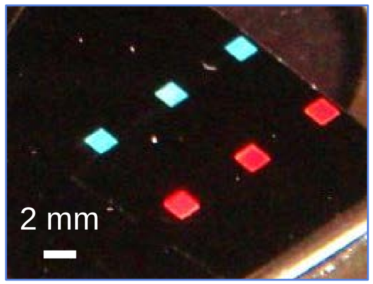



## Bioinspiration –
new functionality, beyond Nature

***High temperature***

Potyrailo, Carpenter, et al., *J. Opt.*, **2018**

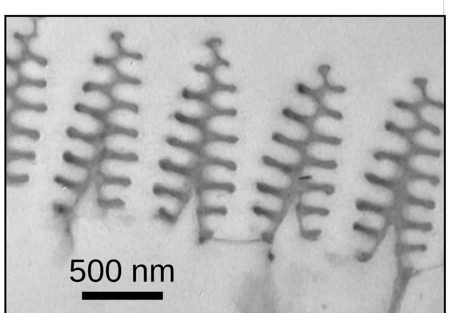



## Biomimetics –
recreation of observed functionality

***Room temperature***

Potyrailo et al., *Nat. Commun.* **2015**

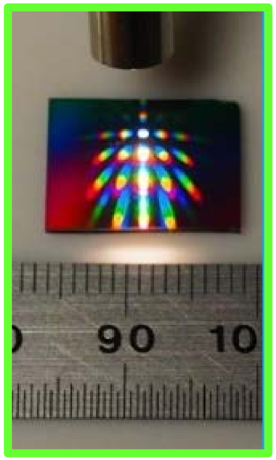



## Biomimicry –
**imitation of biological systems**

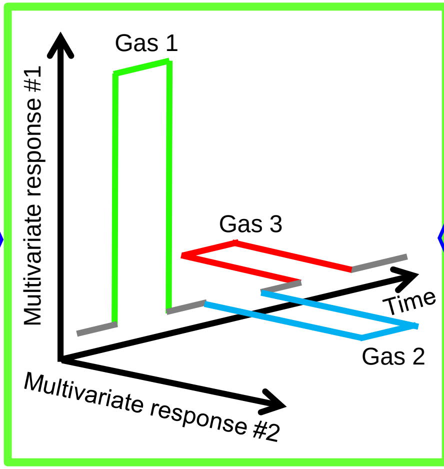
Potyrailo et al., *Nat. Photon.* **2007**

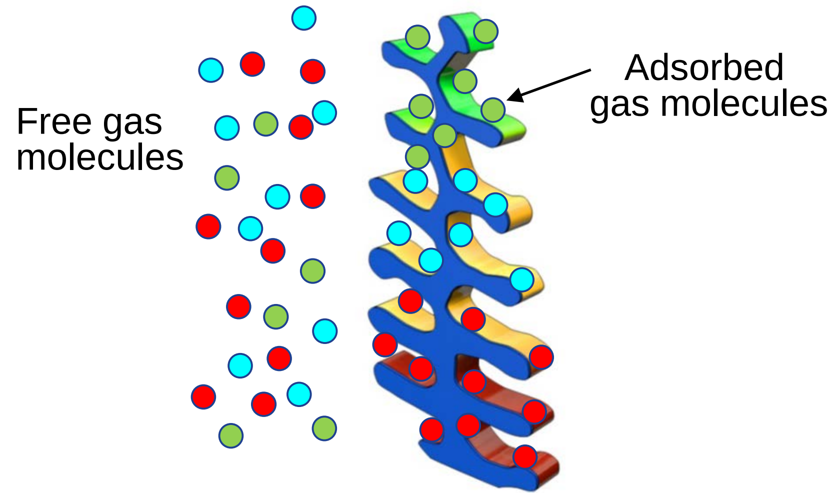
# Multi-gas detection using bio-inspired multivariable photonic sensors

**Our approach:**
Multivariable gas sensors



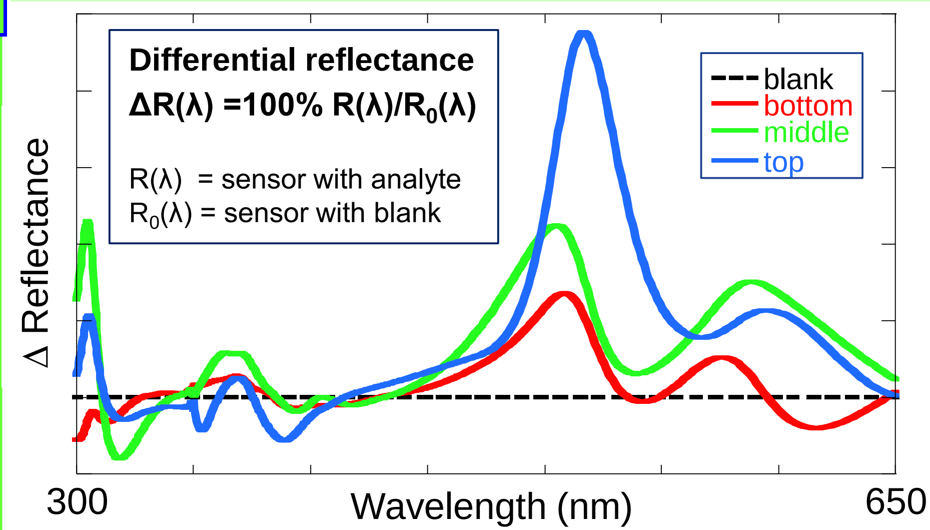

**Performance need:**
Multi-gas discrimination




**Design rules for gas-selectivity control**

- Spatial orientation of surface functionalization
- Chemistry of surface functionalization
- Extinction and scattering of nanostructure

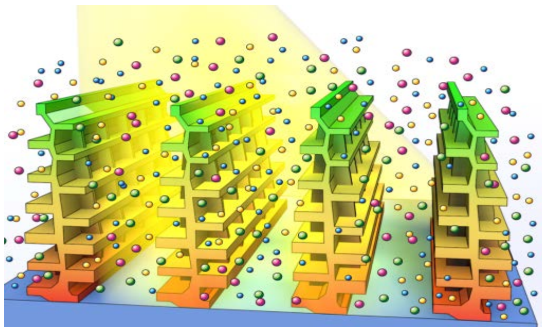



Potyrailo et al. *Nature Photonics* **2007**
Potyrailo et al., *Proc. Natl. Acad. Sci. U.S.A.* **2013**
Potyrailo et al. *Nature Communications* **2015**

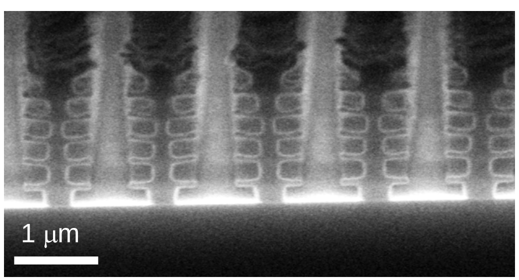
imagination at work

# Advancing design rules of nanostructures for high temperature gas-sensing applications

## Selectivity control for vapors at room temp.

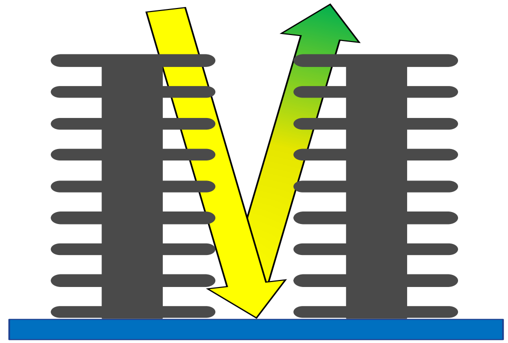


- Polymeric nanostructure
- Absorption and adsorption of vapors

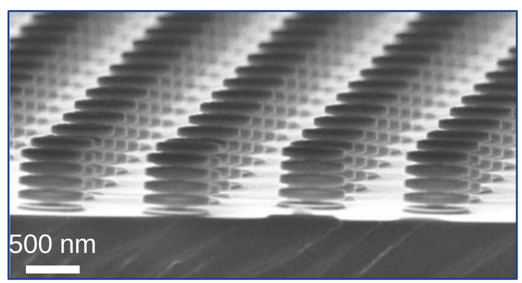



Potyrailo et al., *Nat. Commun.* **2015**

## Selectivity control for gases at high temp.

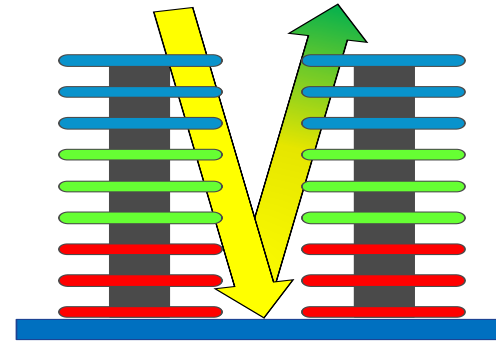


- Inorganic nanostructure
- Catalytic reactions of gases

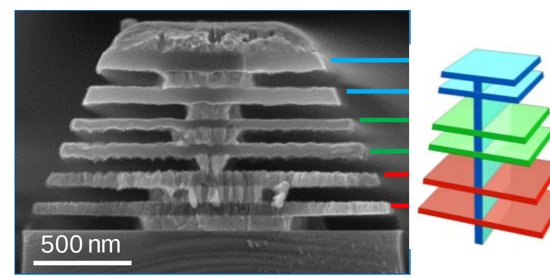



Potyrailo, Karker, Carpenter, Minnick, *J. Opt.*, **2018**

## Interference rejection control

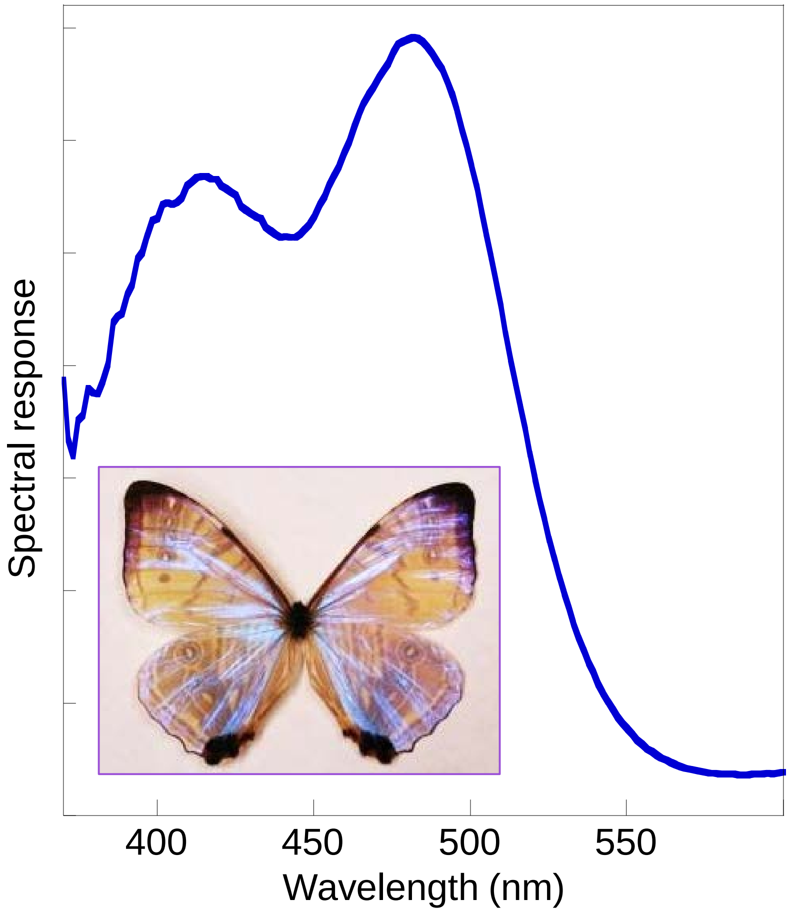


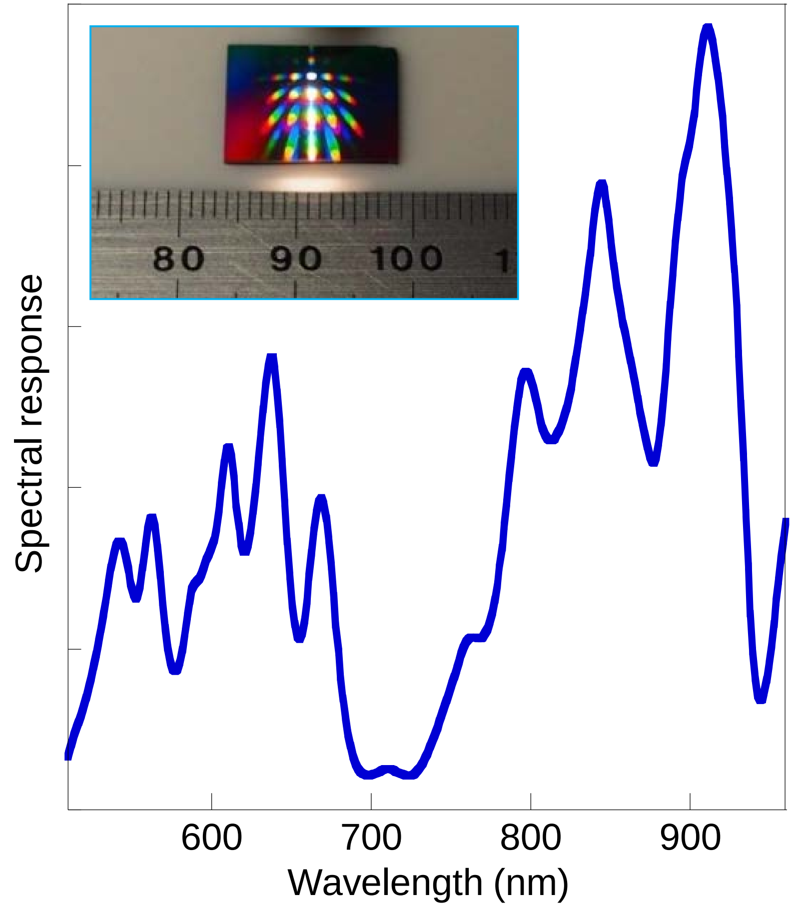
- Multi-material inorganic
- nanostructure
- Catalytic reactions of gases




Potyrailo, *Chem. Rev.* **2016**

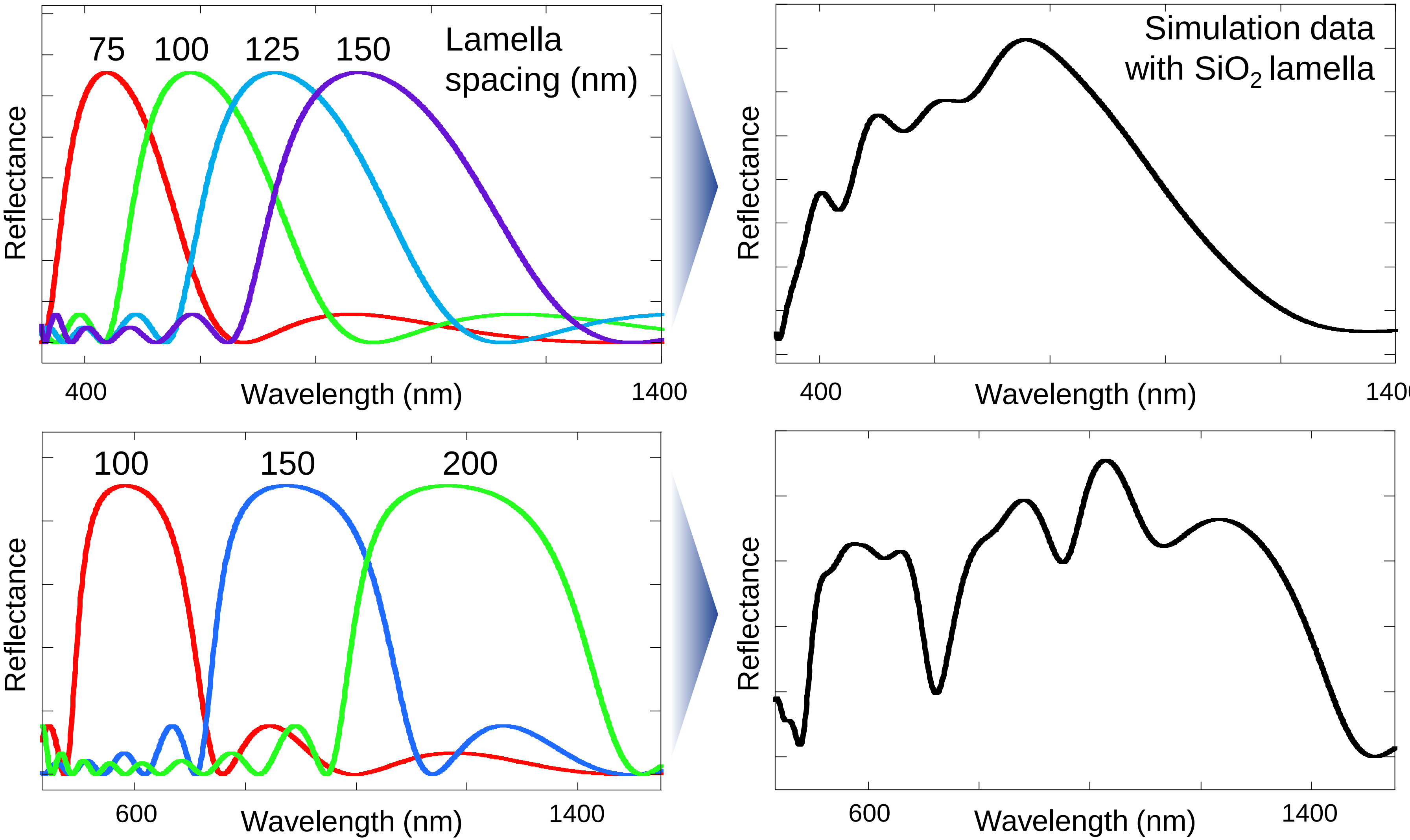
# Needed diversity in spectral response for gas discrimination



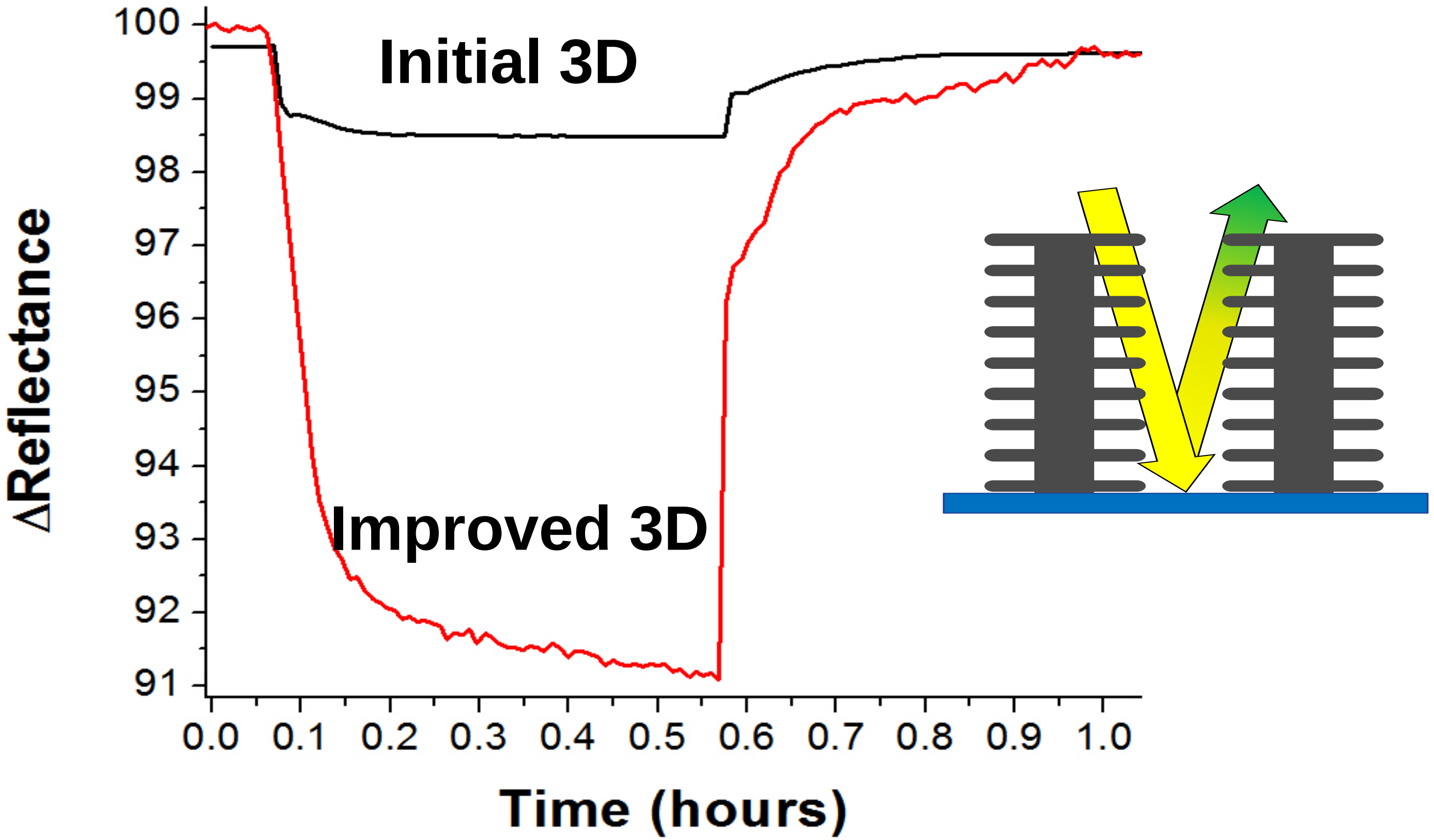

Diverse spectral response
facilitates discrimination between different gases

# Gas-discrimination control




Diverse spectral response using different lamella spacing for discrimination between different gases

# Sensitivity control

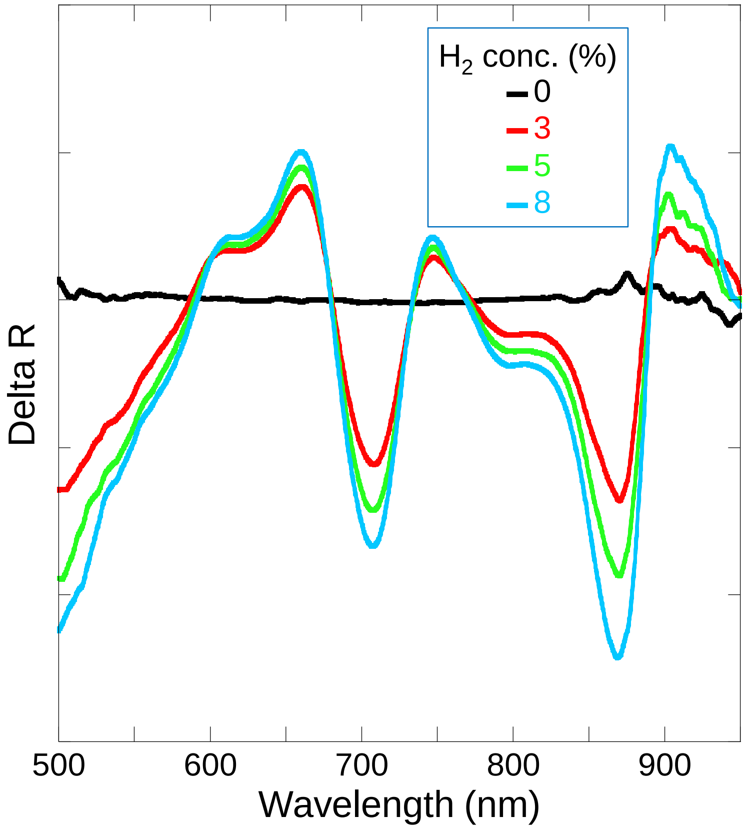



Sensitivity boosted by seven fold by
- material selection
- 3D structure design

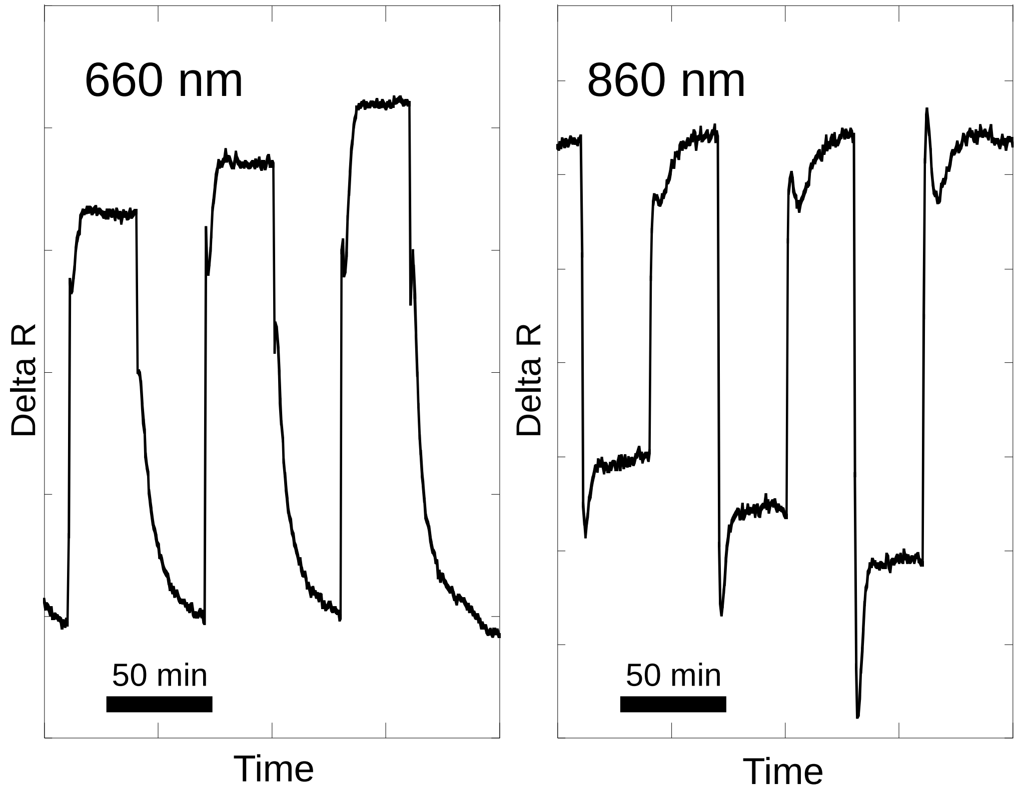
Exposure to 8% $H_2$

# Example of $H_2$ detection

## $H_2$ spectral response




## $H_2$ response: dynamics

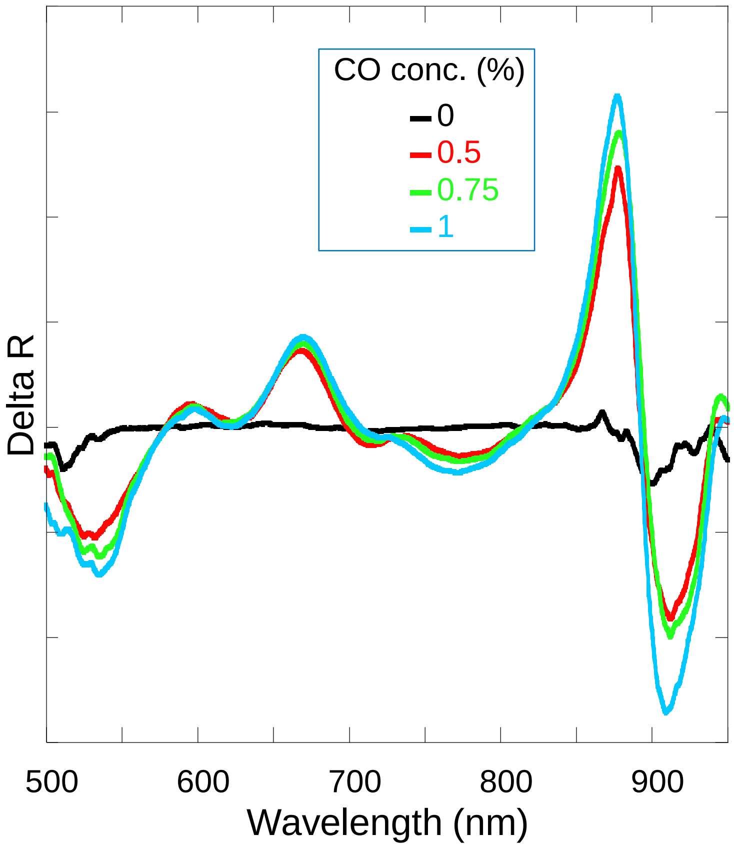



Diverse spectra and dynamics uncover different response mechanisms in nanostructure

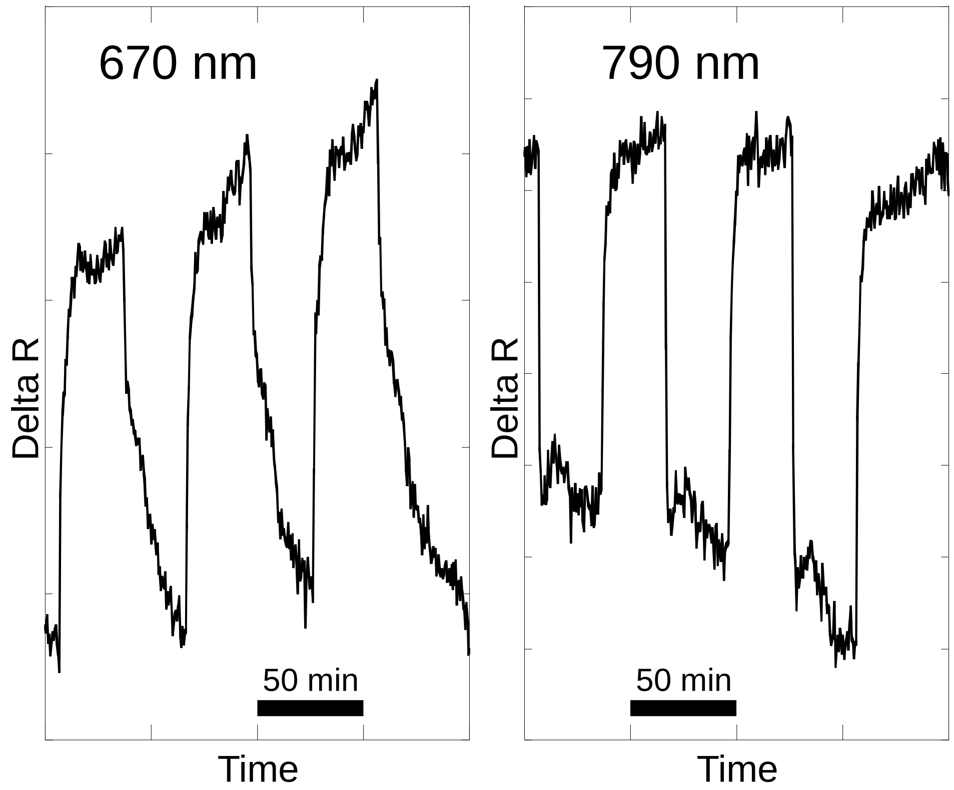
Potyrailo, Karker, Carpenter, Minnick, *J. Opt.*, **2018**

# Example of CO detection

## CO spectral response




## CO response: dynamics

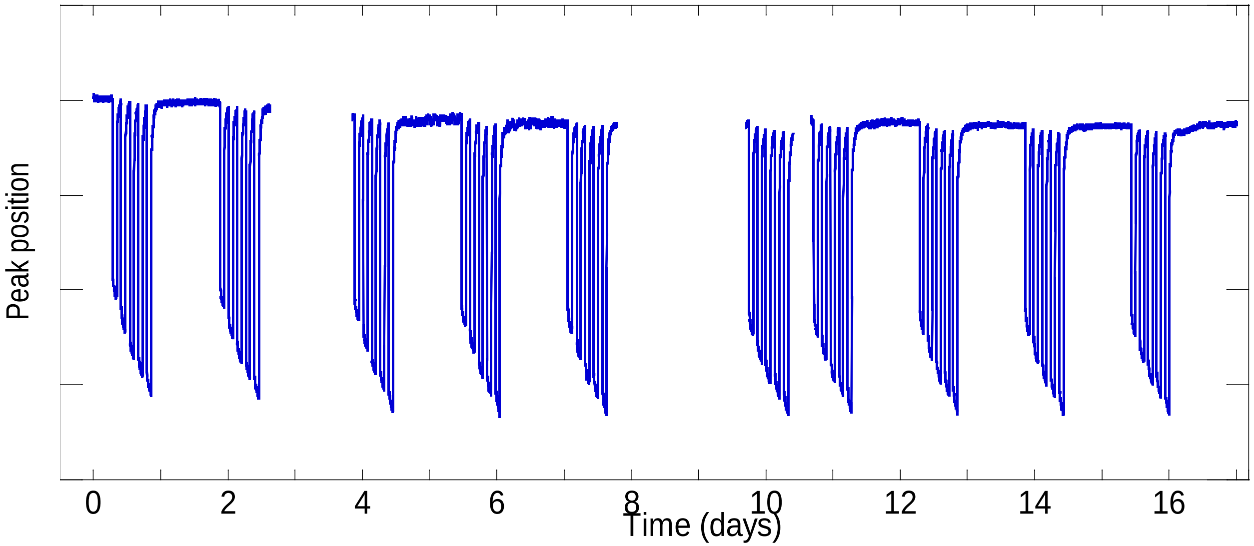



**Diverse spectra and dynamics uncover different response mechanisms in nanostructure**

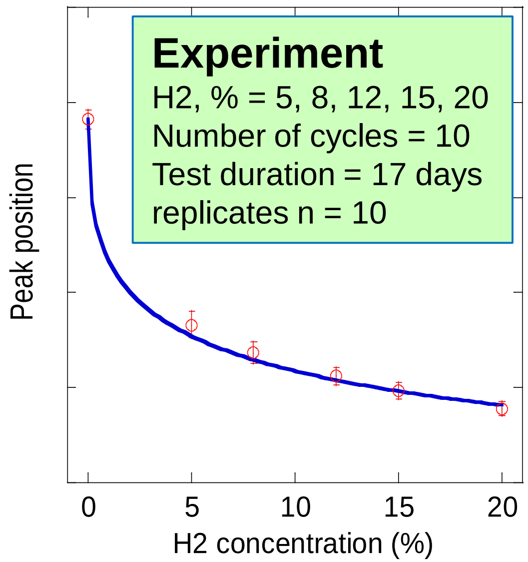
Potyrailo, Karker, Carpenter, Minnick, *J. Opt.*, **2018**

# Initial stability tests: univariate response

**Peak position of one of spectral bands in a planar (control) sensor film**

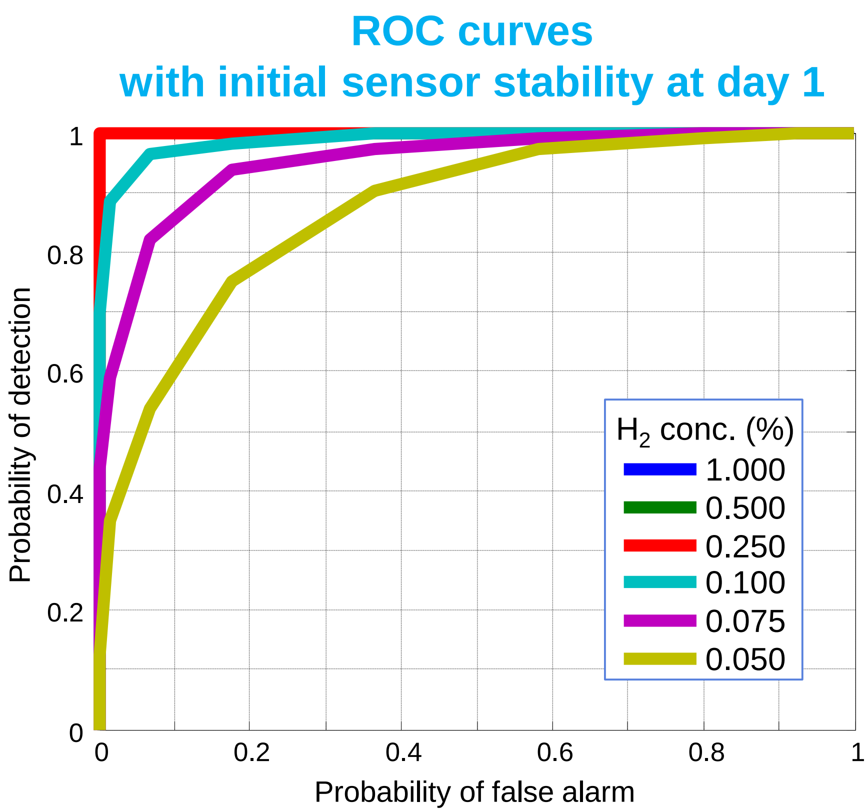


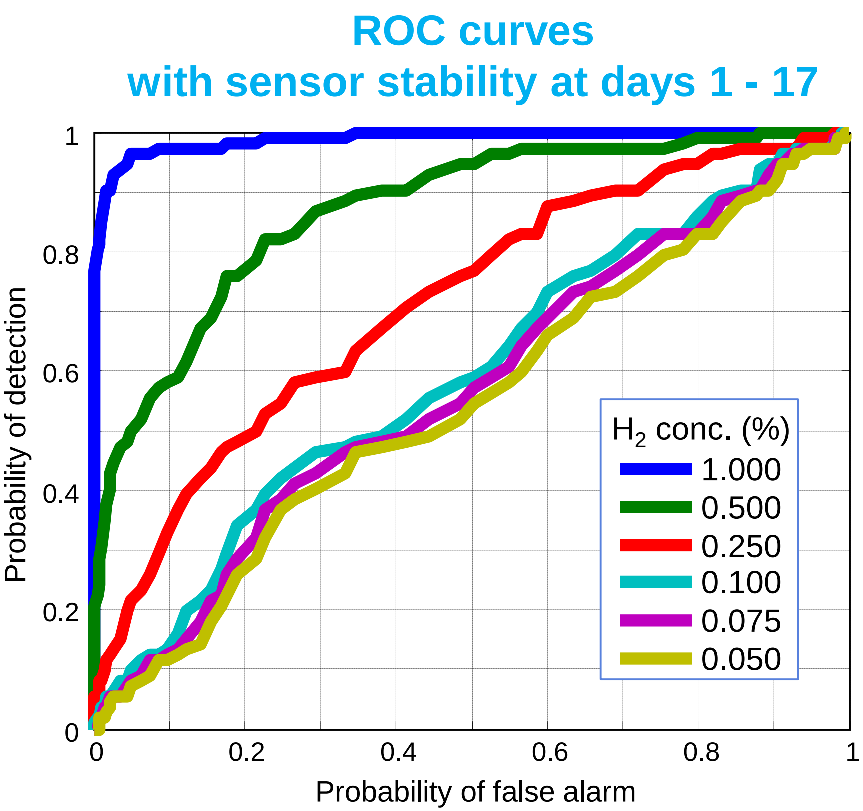

**Calibration curve over 17 days of testing**




Tests with a planar sensor film and analysis of univariate (single output) response allows determination of sensor stability using classical methods

# Receiver Operating Characteristic (ROC) curves



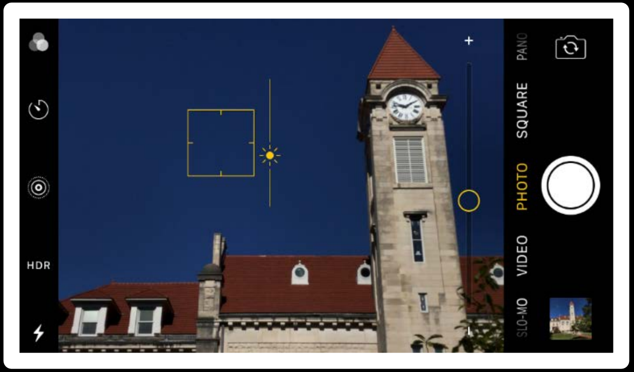




ROC curves illustrate the diagnostic ability of the developed sensor
to reliably detect gas concentrations

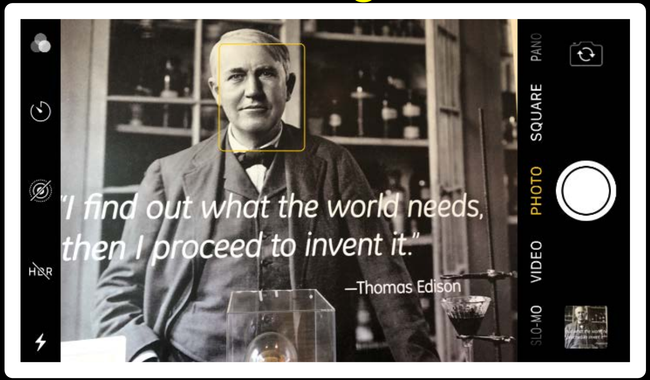
# Software-driven boost of system performance

## Consumer products

**Smart phones: zoom, brightness control**




**Smart phones: face recognition**



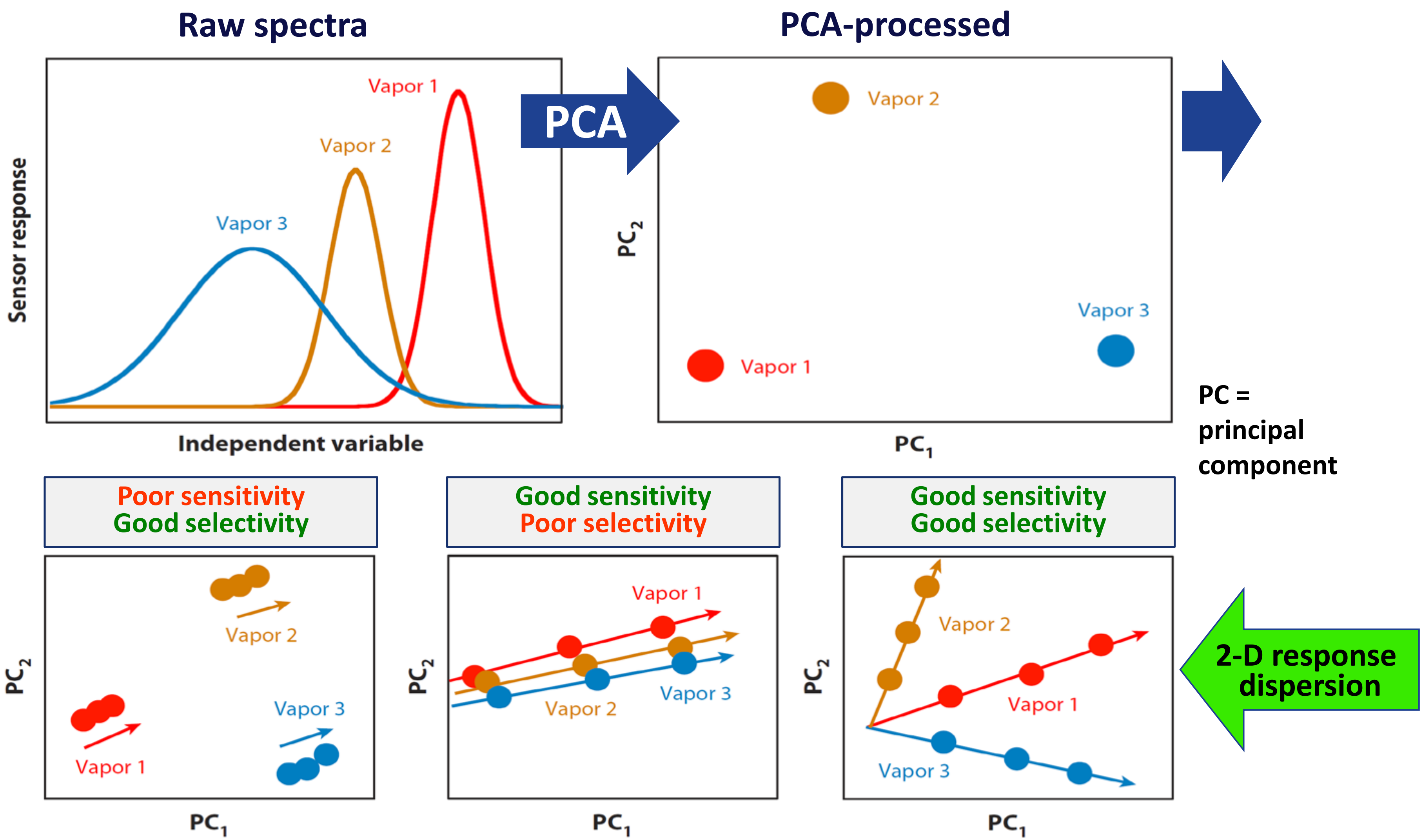

**Car driving modes**


## Electronics analytics

- Principal component analysis (PCA)
- Discriminant Analysis (DA)
- Artificial Neural Network (ANN)
- Hierarchical cluster analysis (HCA)
- Support Vector Machines (SVM)
- Independent Component Analysis (ICA)
- Partial least squares (PLS) regression
- Principal Component Regression (PCR)

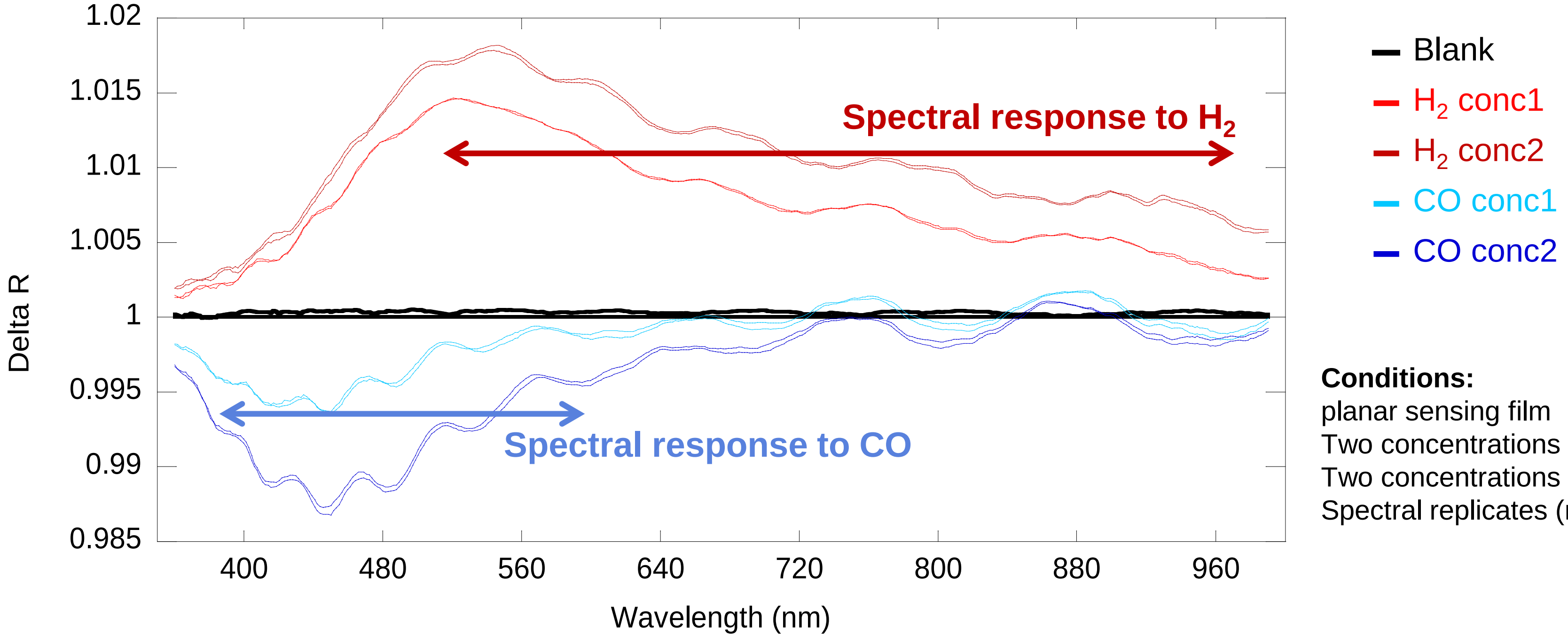
Potyrailo *Chem. Rev*. **2016**

# Multivariate data analysis
## e.g. PCA = Principal Components Analysis




PCA – “classic” tool for reduction of data dimensionality and noise

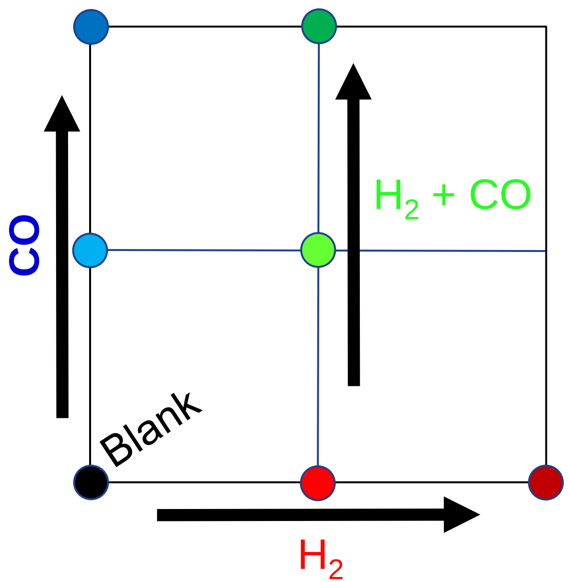
# Initial discrimination between individual $H_2$ and CO gases

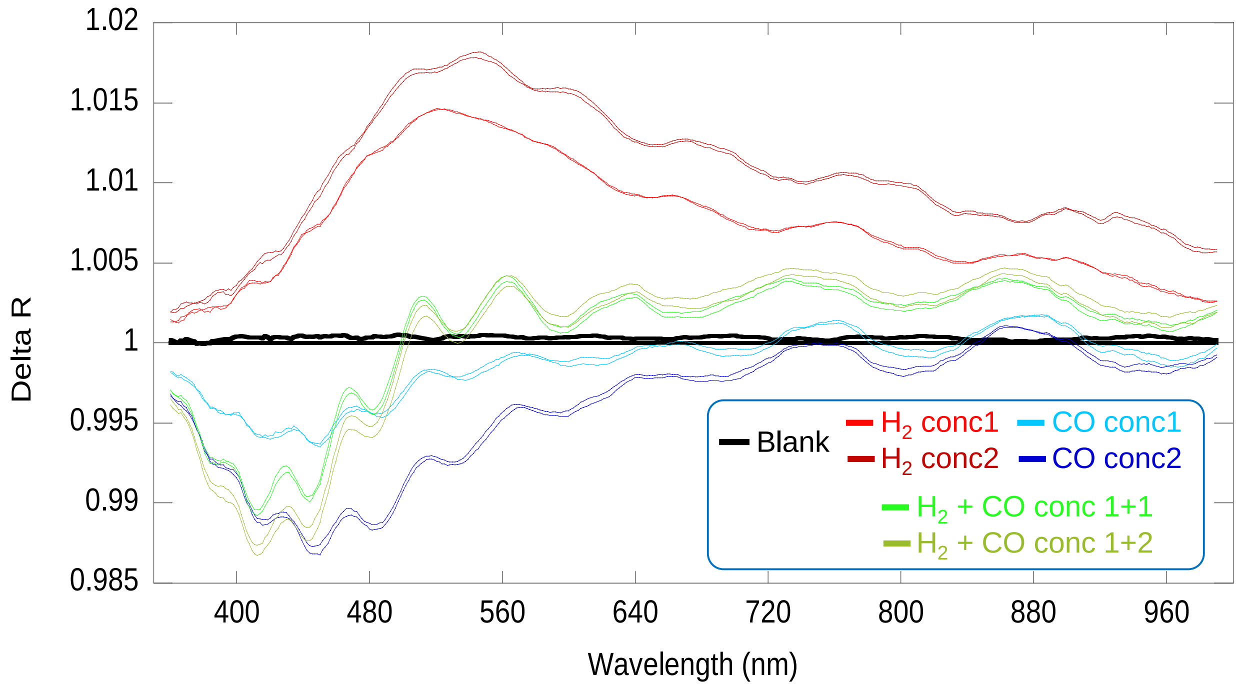



**Conditions:**
planar sensing film
Two concentrations of H2
Two concentrations of CO
Spectral replicates (n=2)

Different spectral regions of optical response of a single sensing to $H_2$ and CO gases should allow discrimination of two gases

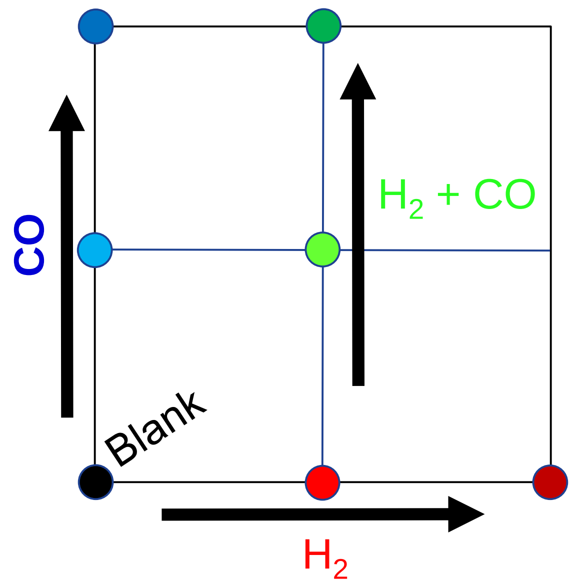
# Initial discrimination between individual and mixtures of $H_2$ and CO gases

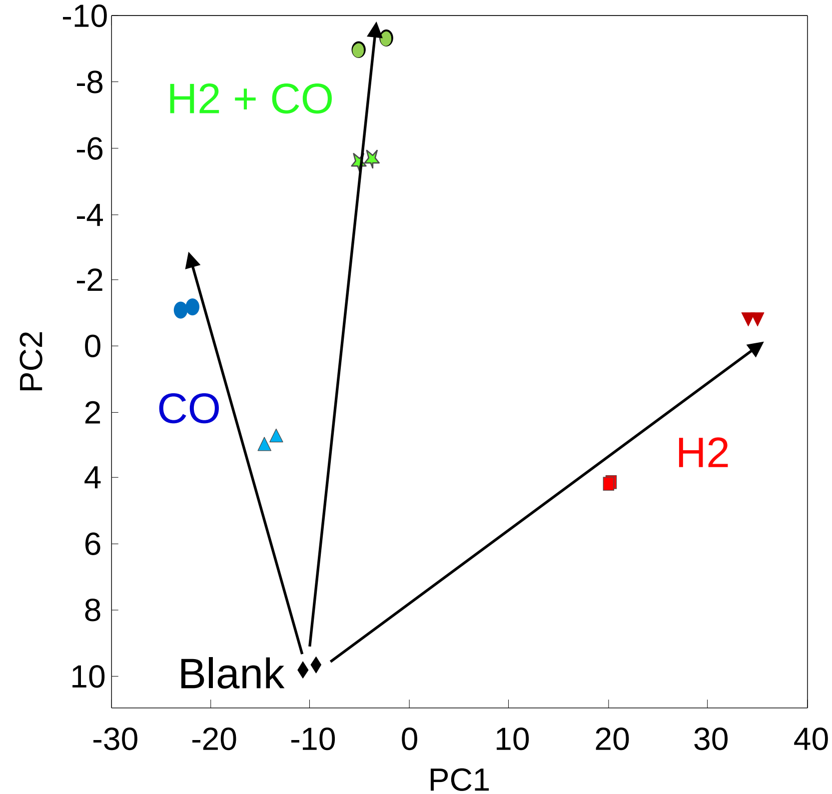



Different spectral regions of optical response of a single sensing to $H_2$ and CO gases should allow discrimination of two gases

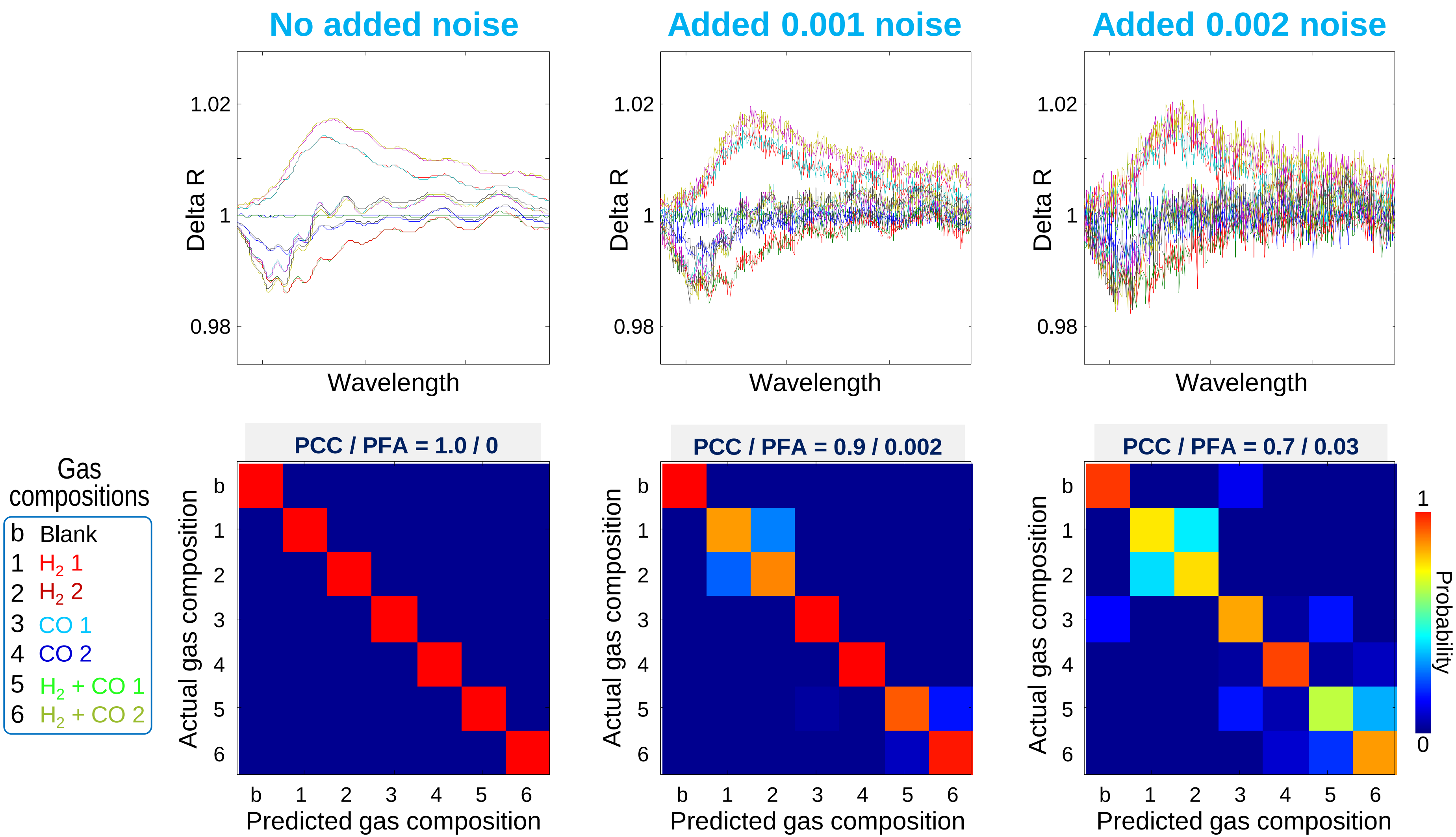
# Initial discrimination between individual and mixtures of $H_2$ and CO gases




Different spectral regions of optical response of a single sensing to $H_2$ and CO gases allow discrimination of two gases

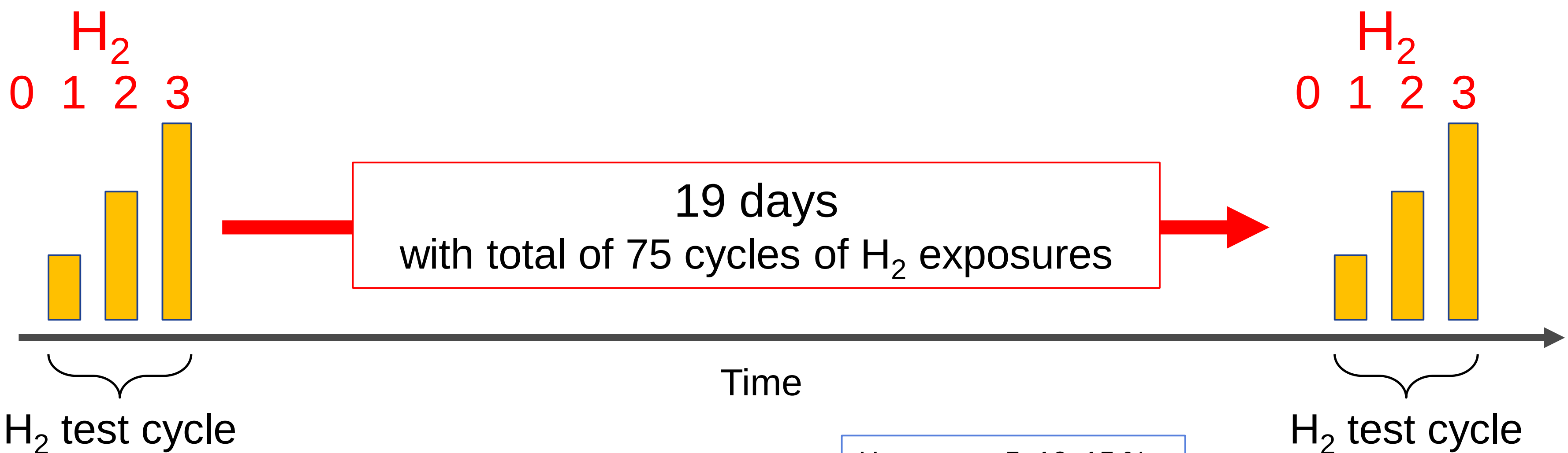
# Confusion matrix analysis

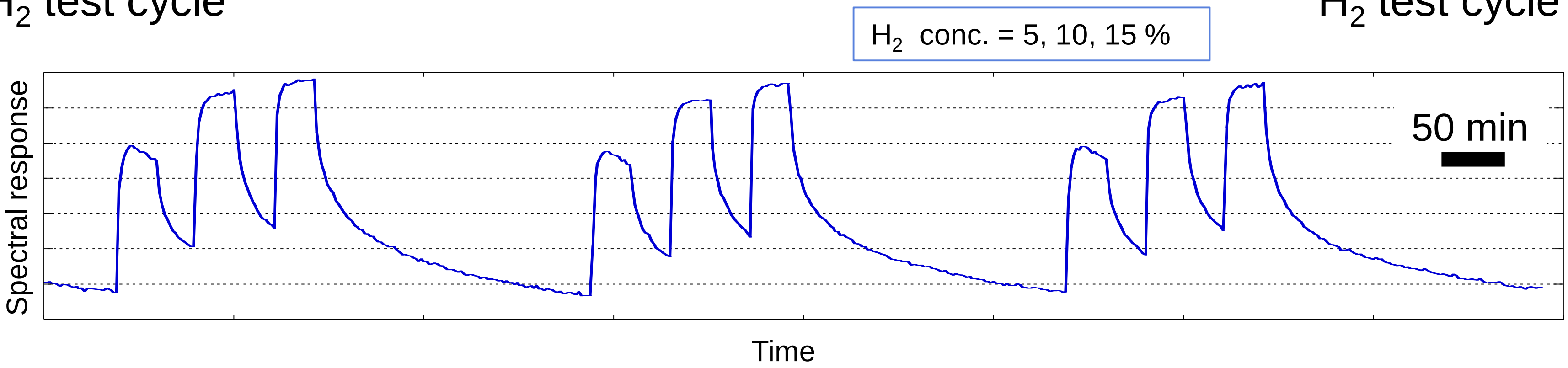



Visualization of quality of prediction of classes

PCC = probability of correct classification;
PFA = probability of false alarm

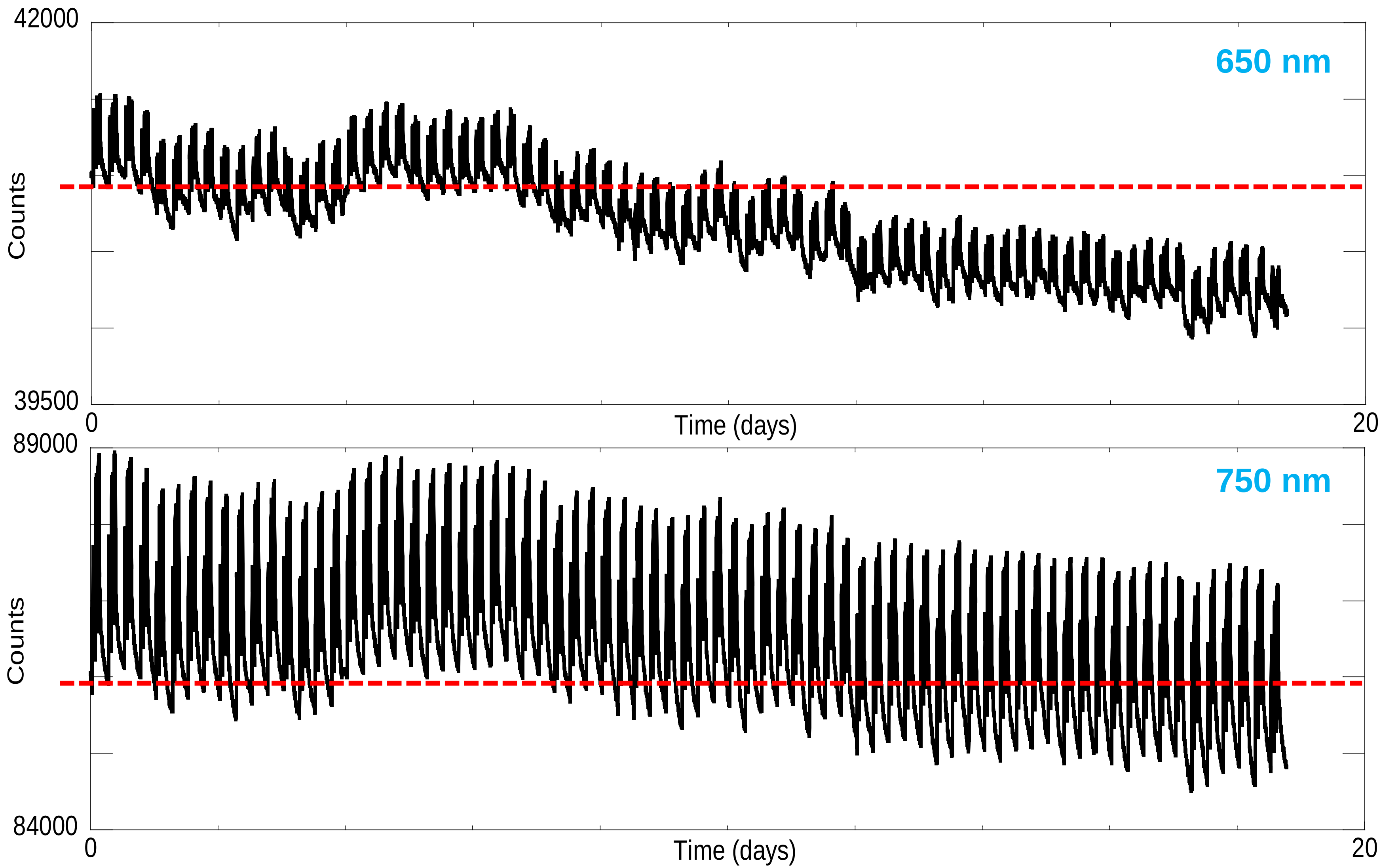
# Long-term response stability testing



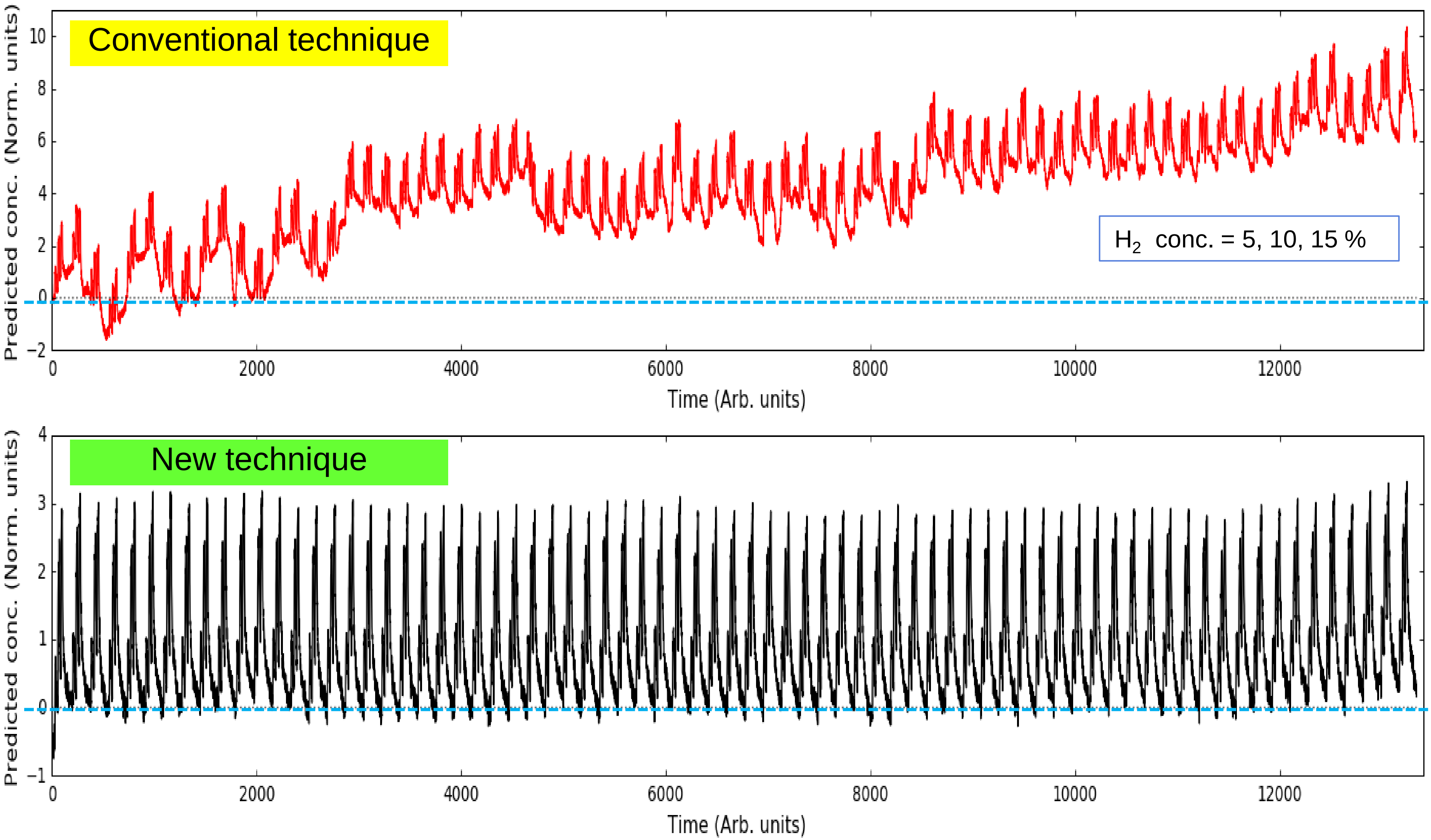

Planar sensor film and analysis of multivariate (many wavelengths) response allows determination of sensor stability using new machine learning methods

# Raw sensor response to $H_2$: effects of drift



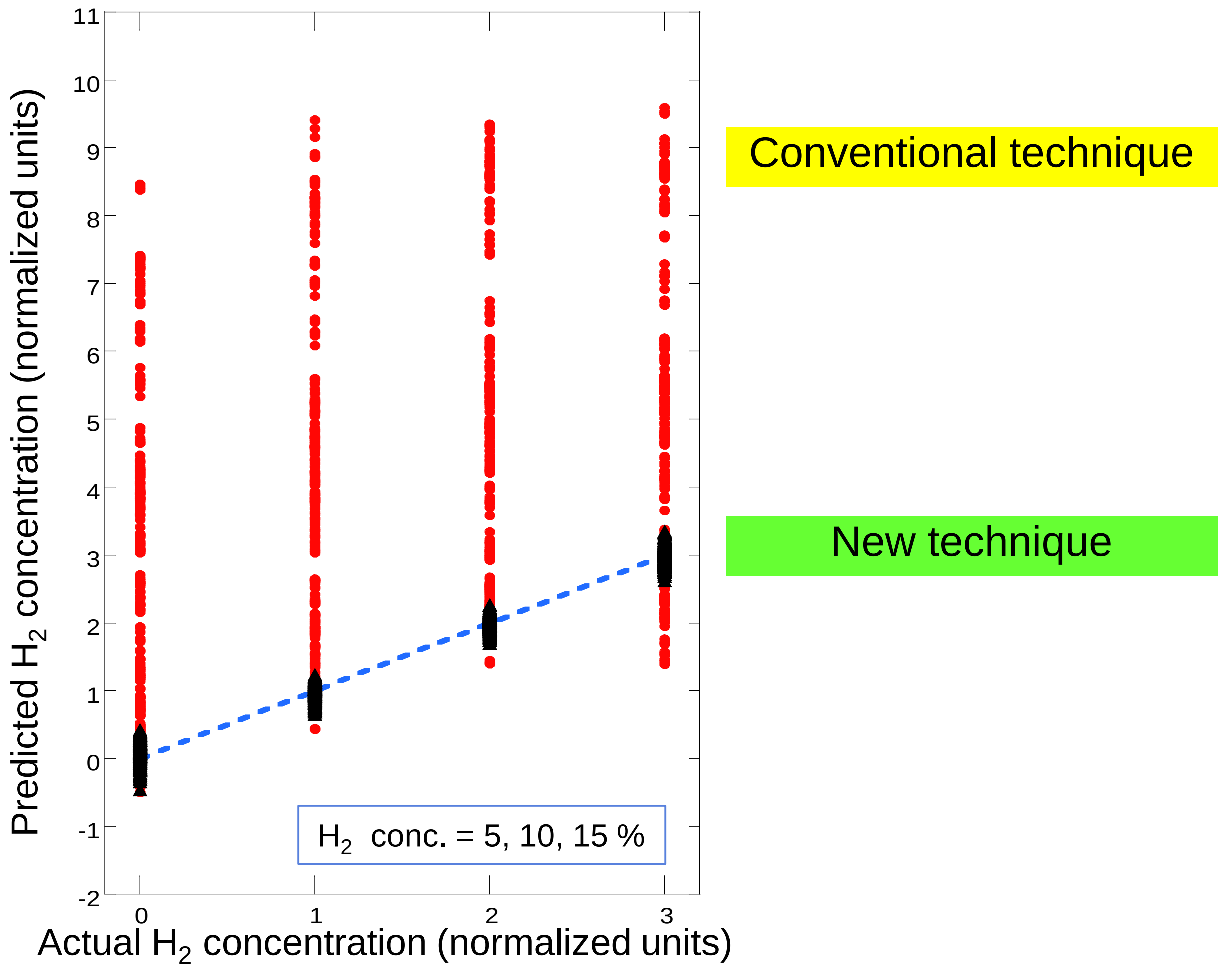

Diverse temporal profiles of drift - possibility for drift correction ?

# Predicted $H_2$ concentrations




Drift correction became a reality using new machine learning tools

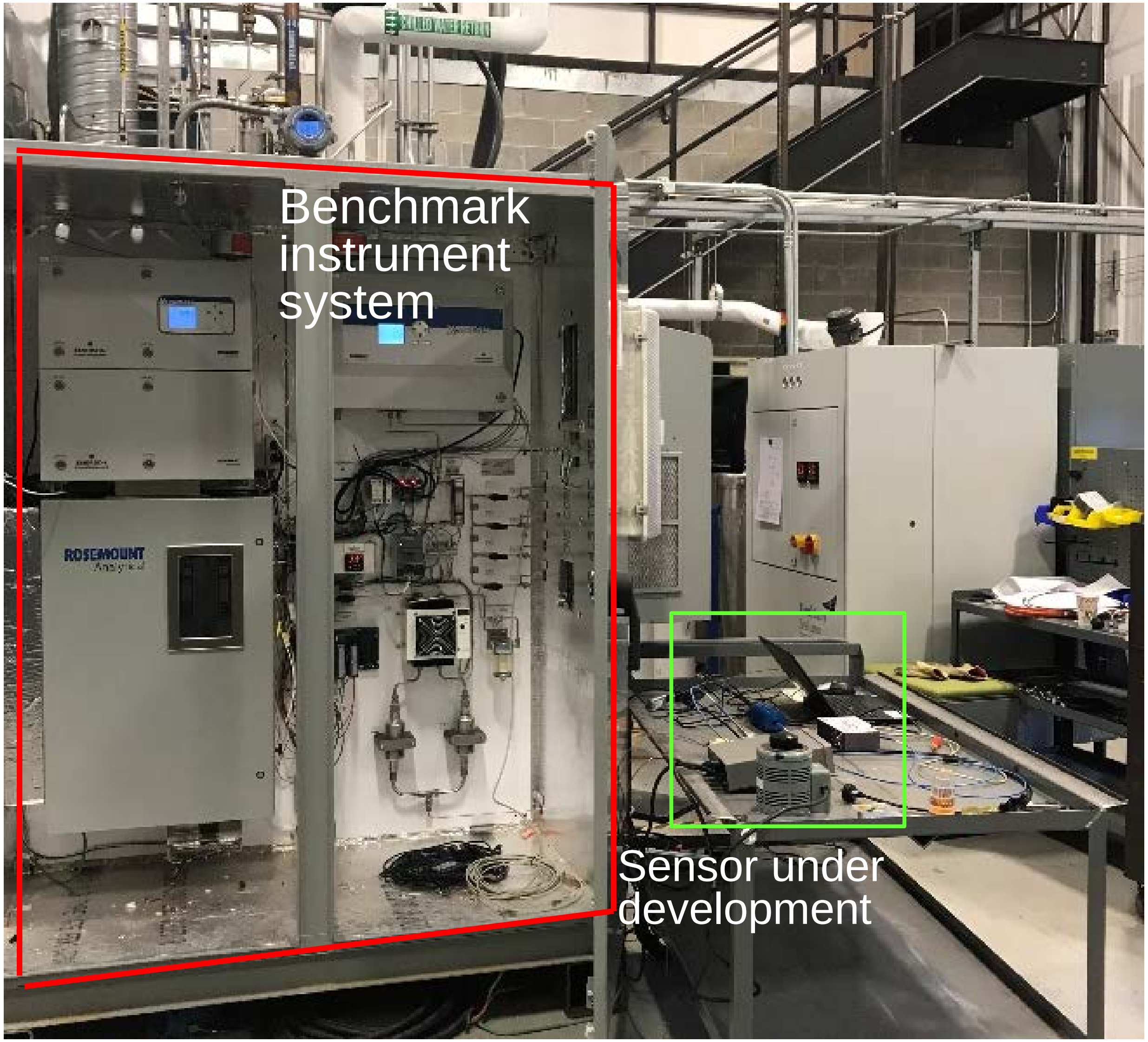
# Correlation of actual vs predicted $H_2$ concentrations




Developed data analytics technique improved the prediction ability of the sensor in detecting and quantifying a single gas

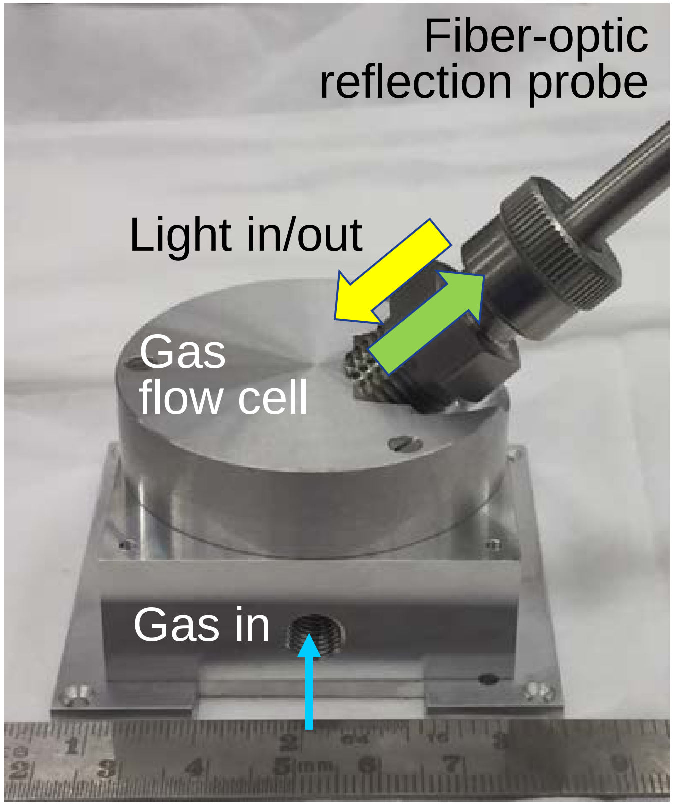
**by more than 10 fold**

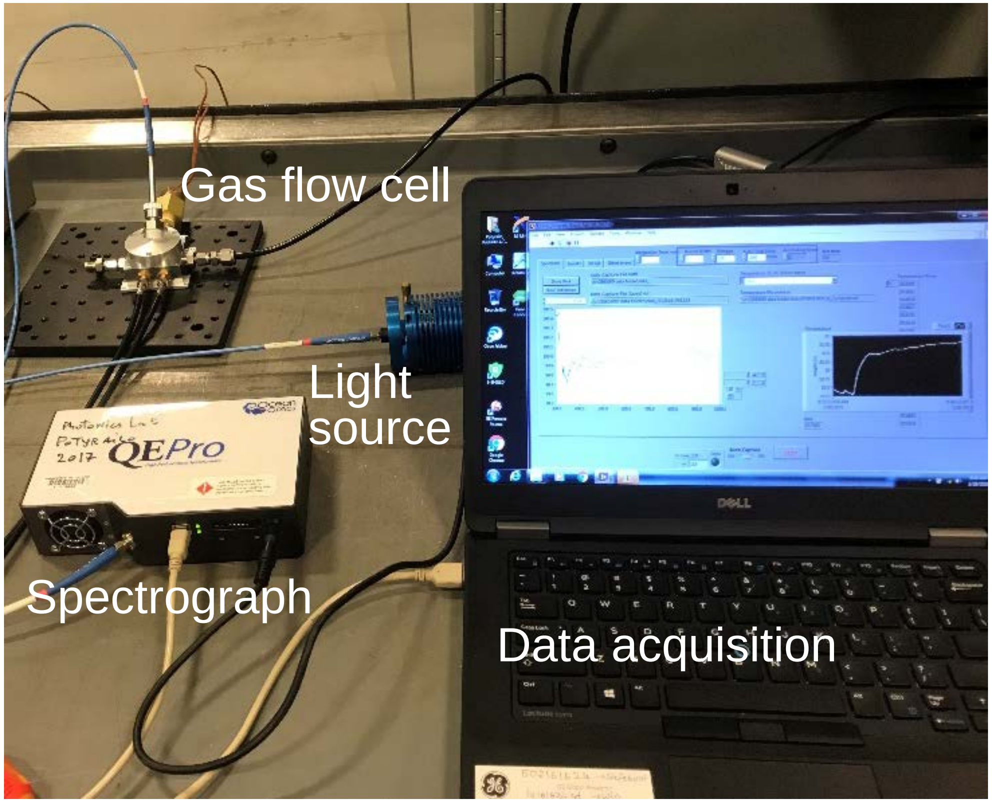
# Initial tests of multivariable sensor at the SOFC factory at GE–Fuel Cells LLC




**Benchmark system:**
Rosemount Analytical (Model X-STREAM Enhanced XEXF)

# Details of multivariable sensor at the SOFC factory at GE–Fuel Cells LLC

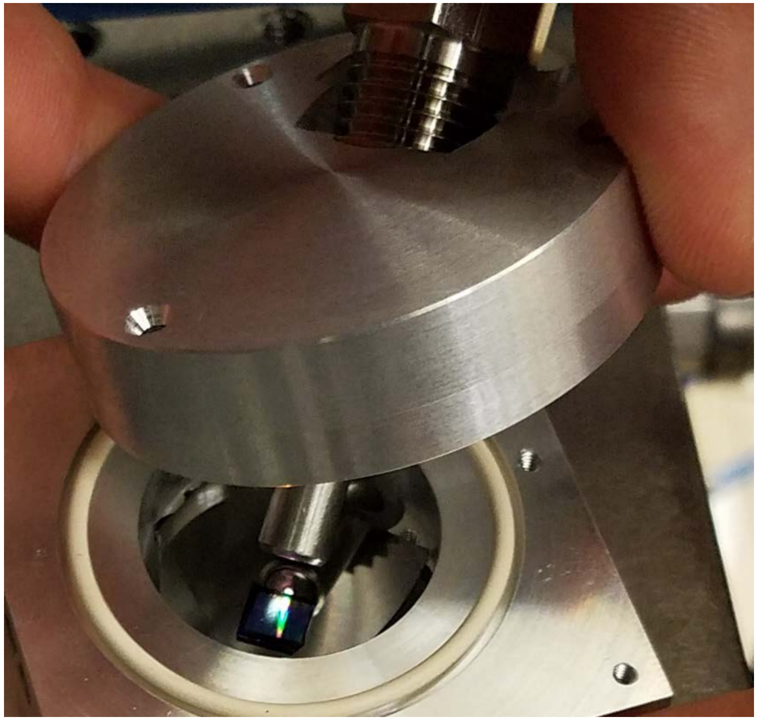


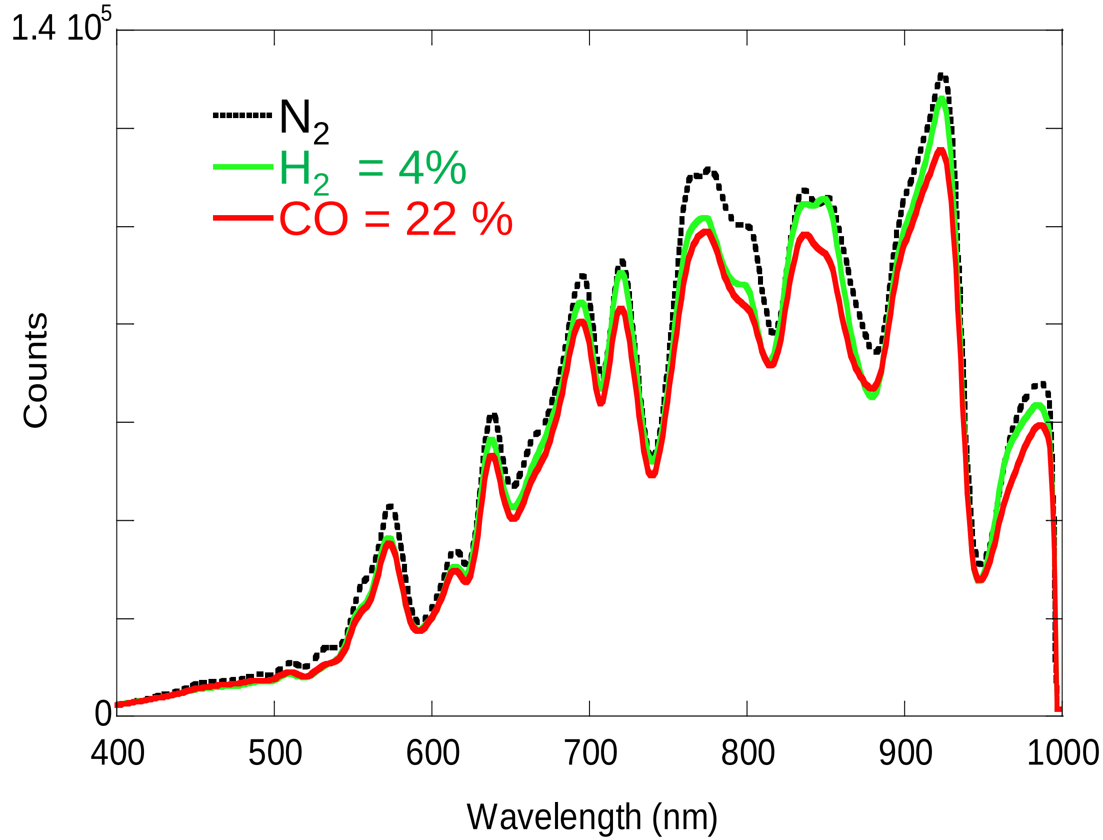




Laboratory components for testing of performance of 3D fabricated nanostructure

# In-situ spectral collection

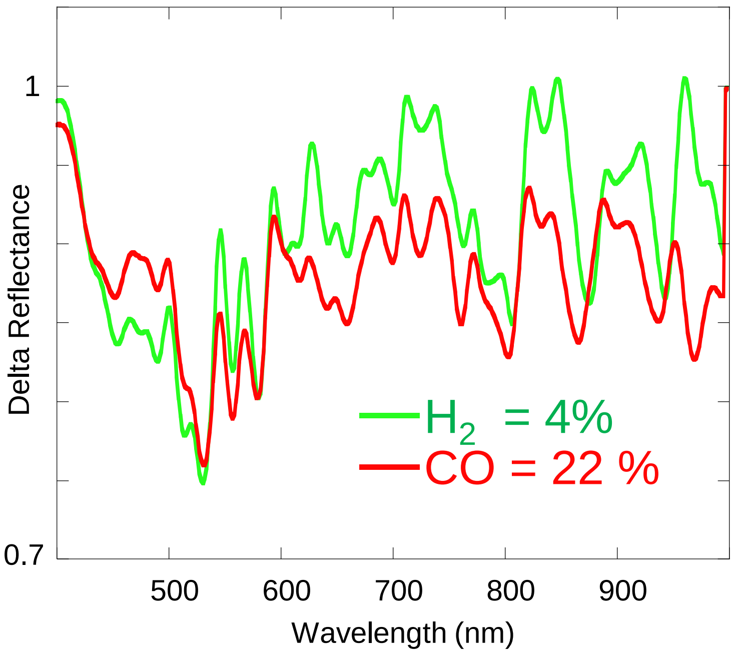
**Sensing chip in gas cell with white light illumination**

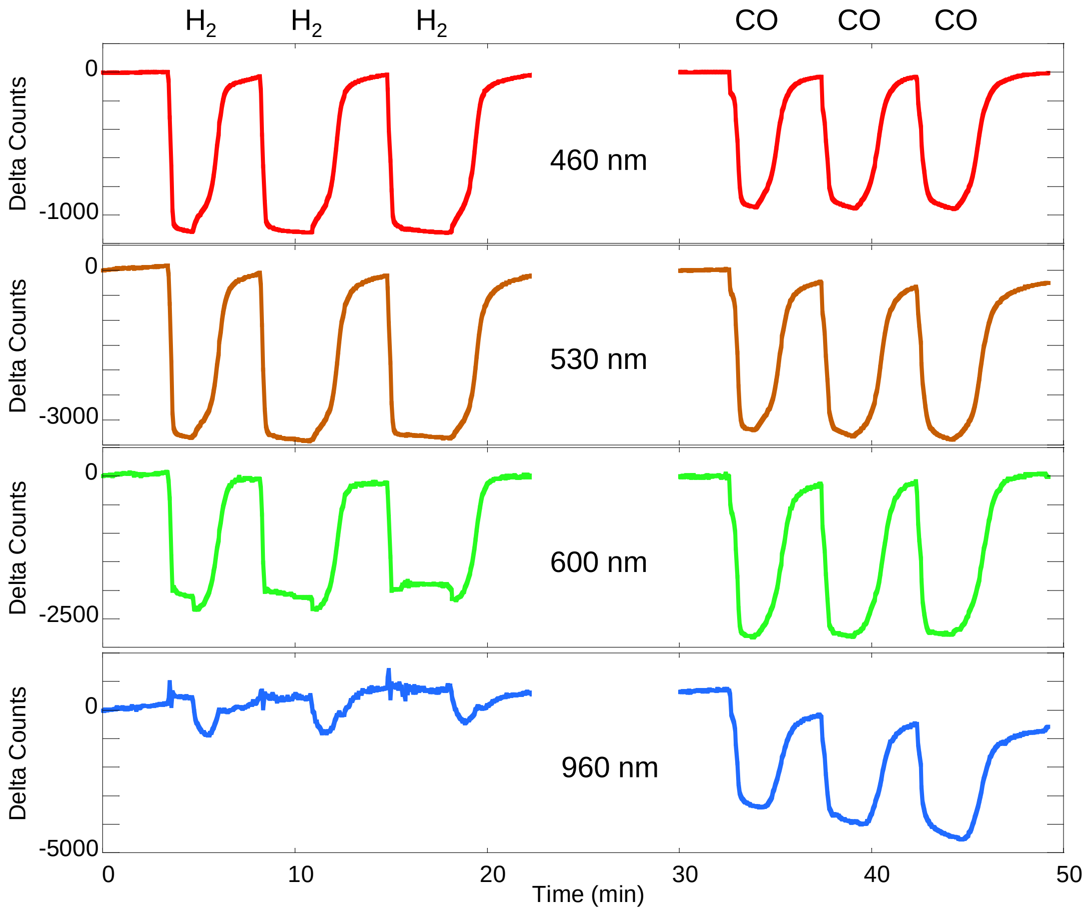





Spectral features of 3D fabricated nanostructure are preserved in the gas cell design for field use

# Initial tests of developed 3D sensing nanostructure at the SOFC factory at GE–Fuel Cells LLC



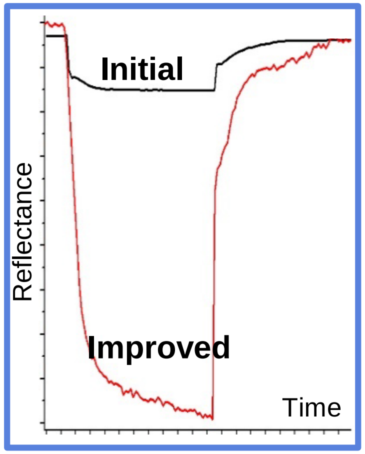




Diversity of spectral features of 3D fabricated nanostructure
For independent quantitation of several gases with a single sensor

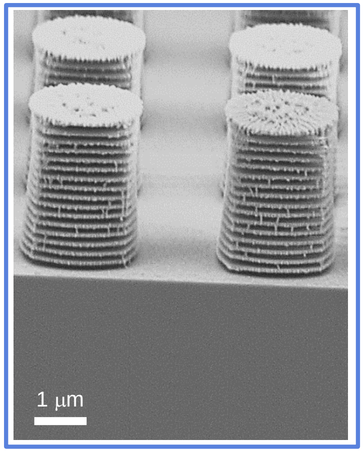
# Summary of photonic multivariable gas sensors: developed capabilities

## This year top FIVE accomplishments

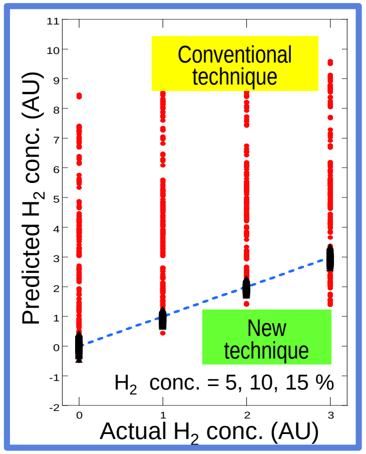
**Sensitivity control**



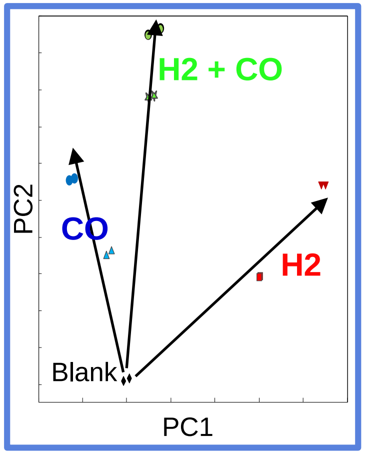

**Selectivity control**



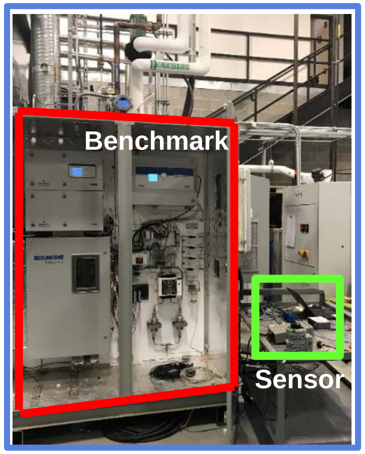

**Sensor stability**




**Detection of gas mixtures**




**Initial field validation**




## Next steps:

- Summarize and document developed design rules for photonic multivariable sensing at high temperature
- Complete validation of developed multivariable sensor at the SOFC factory at GE–Fuel Cells LLC

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