# Highly Selective and Stable Multivariable Gas Sensors
## for Enhanced Robustness and Reliability of SOFC Operation

NETL Contract FE0027918

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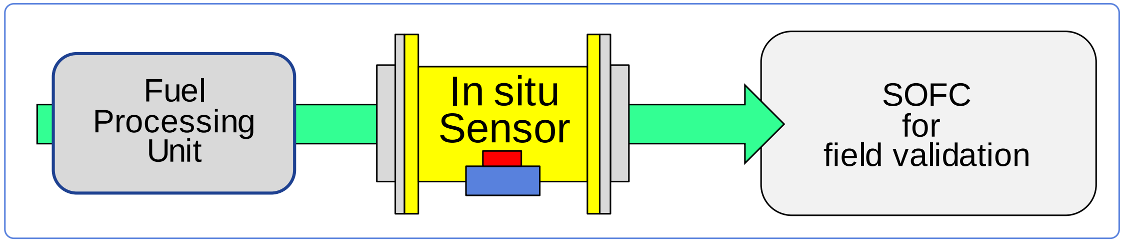
**Background**

**Goals for wide adoption of SOFC**
- needs to improve cost-effectiveness
- enhance operation reliability

**Technical strategy**
- early diagnostics of potential upsets
- ability to operate cells at optimum conditions




**Project objective**

**Phase 1 activities:**
- develop sensing materials
- perform lab tests and field validation

**Phase 1 outcomes:**
- fundamental understanding of multivariable gas sensors at high temperatures
- enable cost-effective and stable sensors for SOFC applications

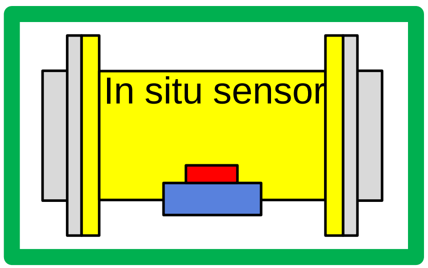
**Technical approach**
- implement new generation of gas sensors (multivariable sensors)
- leverage design rules of multivariable sensors for SOFC monitoring
- dynamic information about SOFC reforming gases

  gases in Phase 2: 15-20% $H_2$, 10-20% CO, 5-20% $CO_2$, 2-15% $CH_4$, 40-60% $H_2O$

  gases in Phase 1 are subset from Phase 2

# Proposed sensor vs available offerings

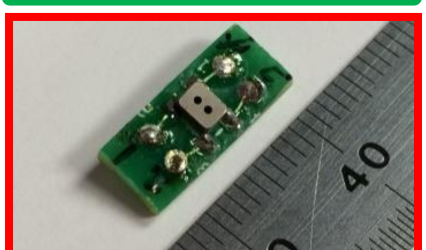
**Available**
$250,000 system,
high selectivity,
extensive sampling,
lab operation




**Proposed**
$10,000 - 20,000 system,
high selectivity,
in situ operation
**at high temperature**

## Sensor requirements

- High reliability (accuracy, stability)
- Low initial / operation cost
- Low power consumption




**Available**
$5-10 sensor, $50 – 10,000 system
poor selectivity,
in situ operation
**at ambient temperature**

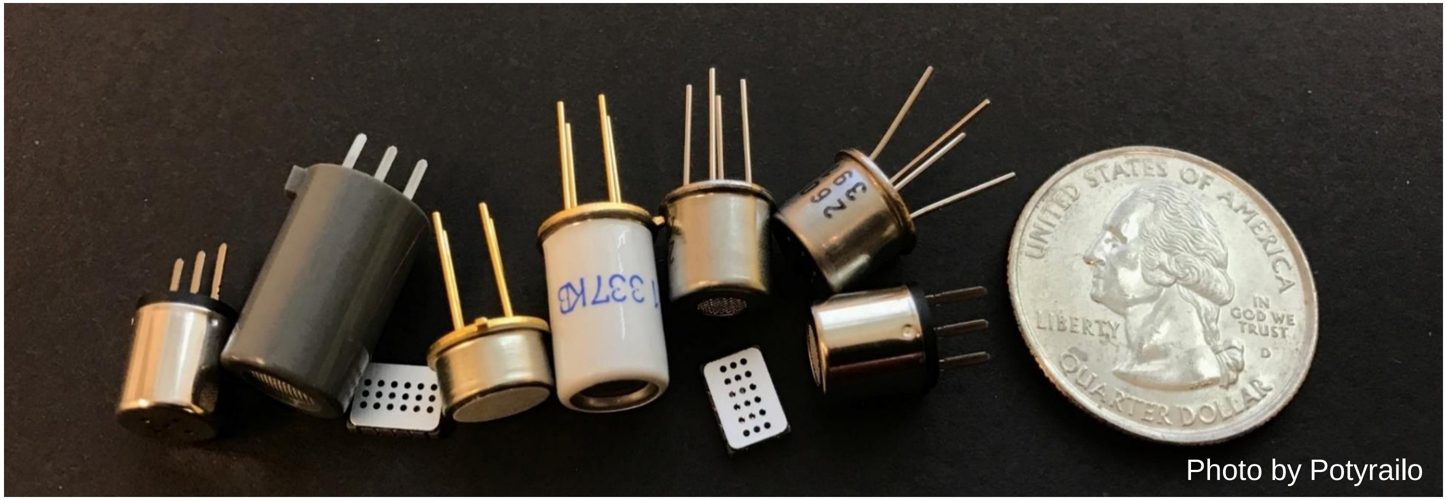
Cost

In Situ

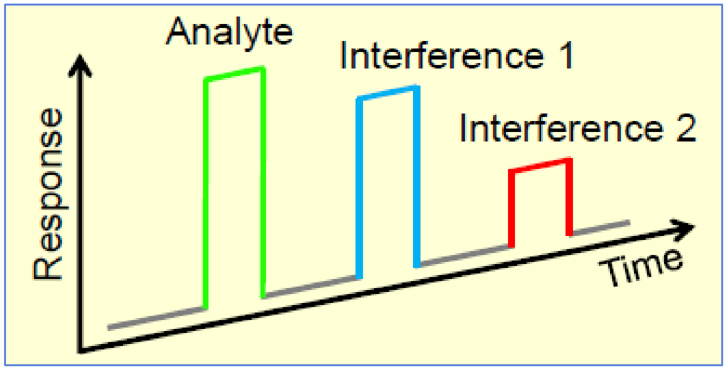
Sampling

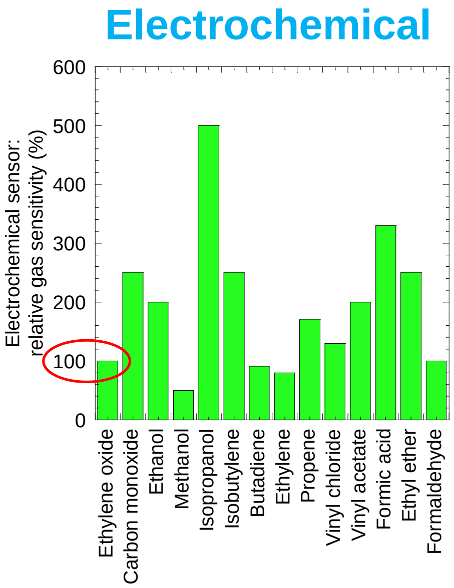
# Commodity gas detection:
## Serving sensing needs in established markets

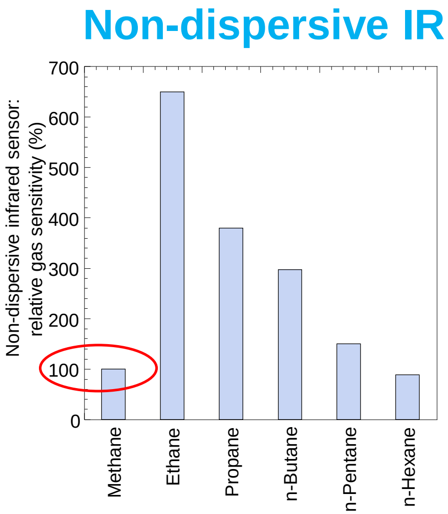
- Mature status-quo technology
- Widely available
- Interchangeable
- Inexpensive



# Commodity gas detection:
## Challenges outside established markets



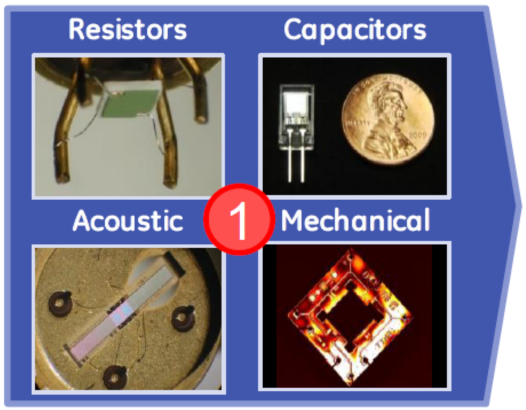



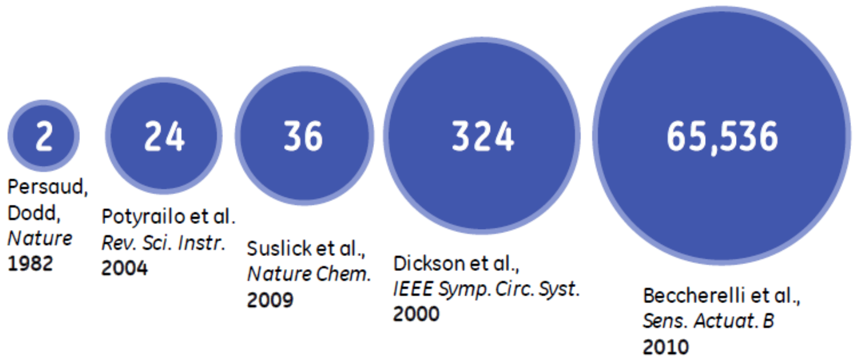




> *"The biggest headaches are caused by interfering chemicals…"*
>
> Lewis, Edwards, *Nature*, **2016**, *535*, 29-31

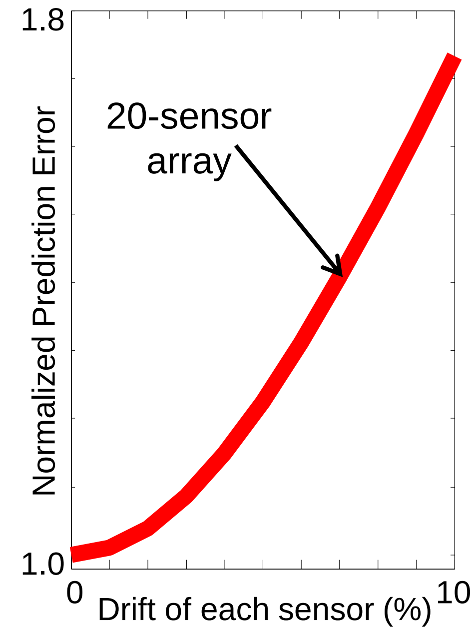
Existing sensors do not meet monitoring demands
**of new growing markets**

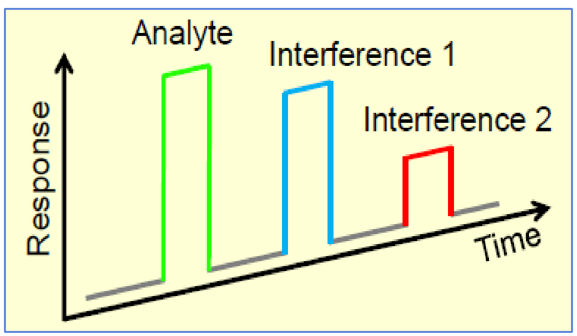
# Sensor arrays as accepted compromise

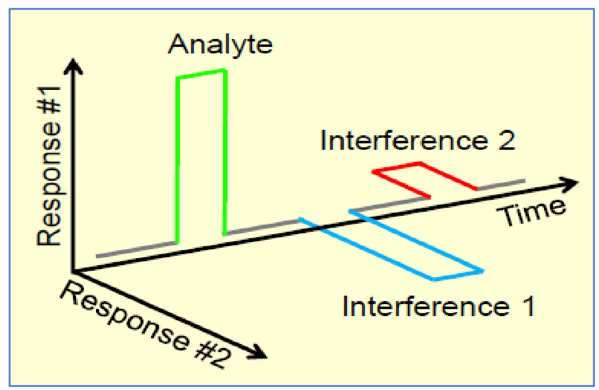



**Stability of sensor arrays**



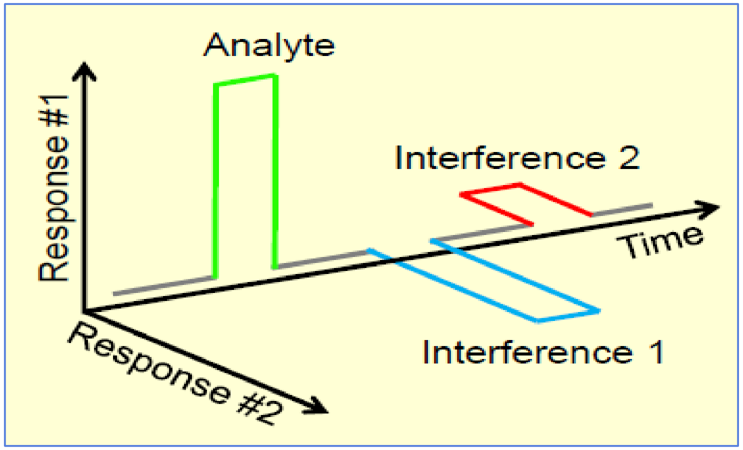




Sensor arrays:
Compromise between selectivity of sensor system and system complexity

# Existing approaches for high value gas detection

- •Environmental
- •Homeland Security
- •Industrial Hygiene
- •Petroleum / Biofuel
- •Chemical
- •Agriculture
- •Food & Beverage
- •Pharmaceutical
- •Forensic

## Performance of competing approaches




## Multi-analyzer

## Portable MS

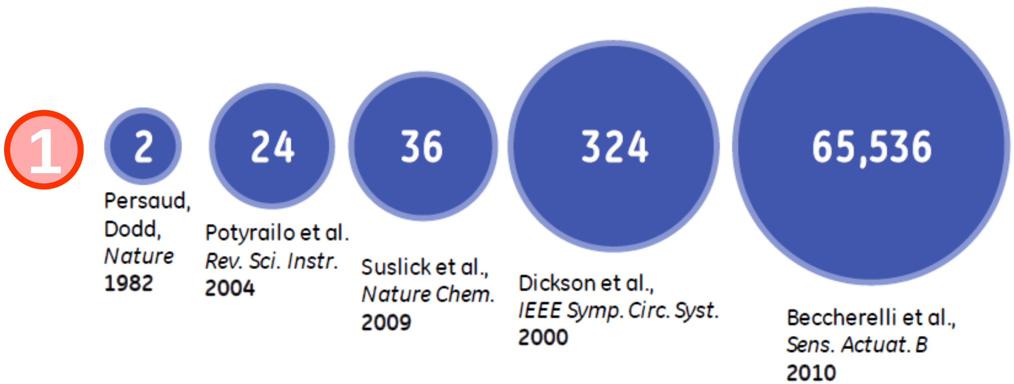
Cooks, Purdue University

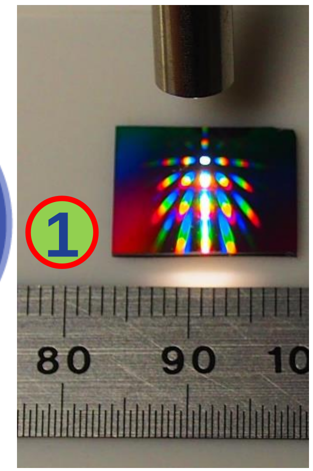
## Portable GC

Pine-environmental.com

Modern approaches for detection of volatiles with high selectivity:
Solving demanding measurement needs with available tools

# Breaking status quo:
# multivariable photonic gas sensors




## Potyrailo et al.

*Nature Photonics* **2007**
*Nature Photonics* **2012**
*Proc. Natl. Acad. Sci. USA* **2013**
*Nature Communications* **2015**
*Chemical Reviews* **2016**

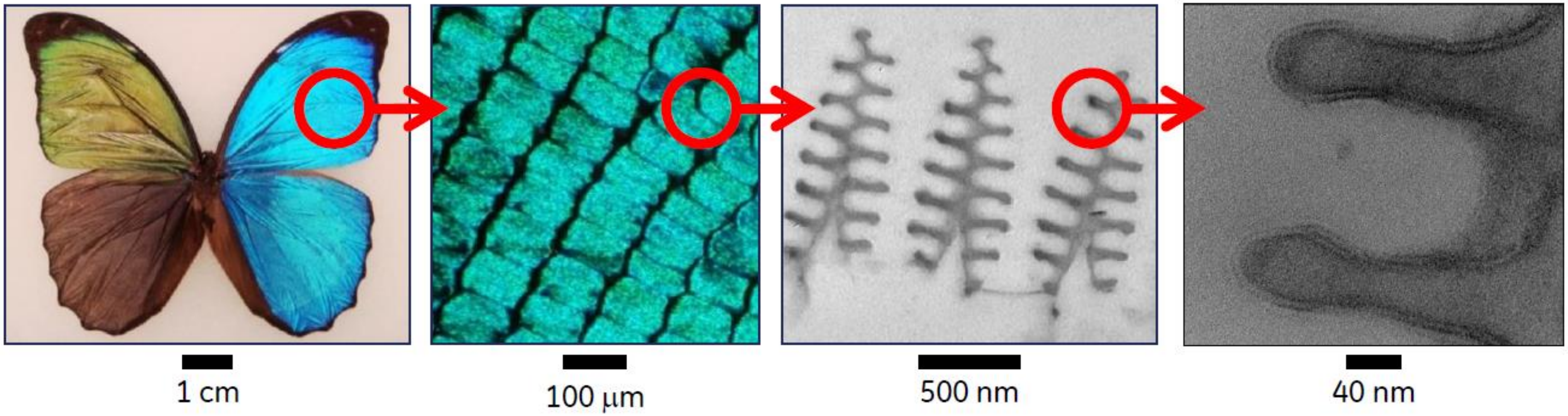
## Carpenter et al.

*Anal. Chem*. **2012**
*Beilstein J. Nanotechn.* **2012**
*ACS Nano* **2014**
*Nanoscale* **2015**

**Individual multivariable sensors:**

- Several independent responses from individual sensor
- Disruptively overcome insufficient selectivity of existing sensors

# Physics of color formation:
## Value for multivariable photonic sensors

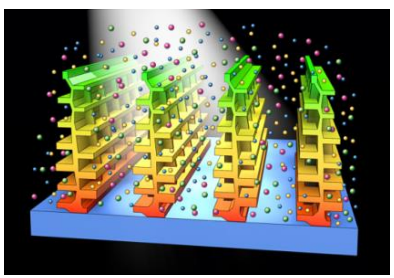



Combined effects of multilayer interference and diffraction produce iridescence in natural *Morpho* butterfly scales


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

# Bio-inspired gas sensors

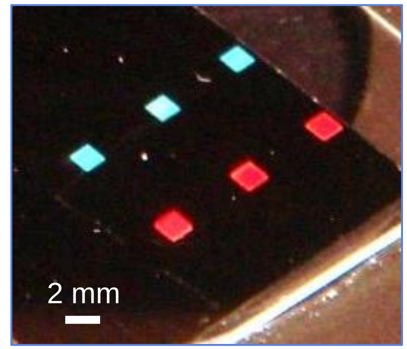
## Natural

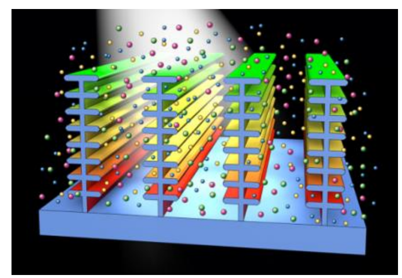


## Design rules for gas-selectivity control

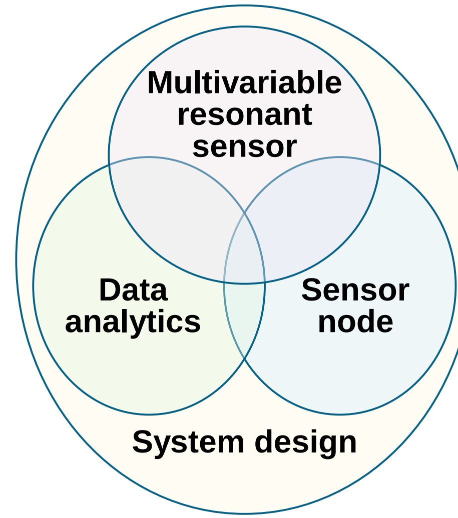
- Spatial orientation of surface functionalization
- Chemistry of surface functionalization
- Extinction and scattering of nanostructure

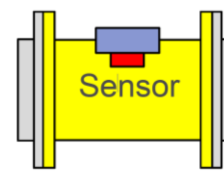
## Bio-inspired



## System concept



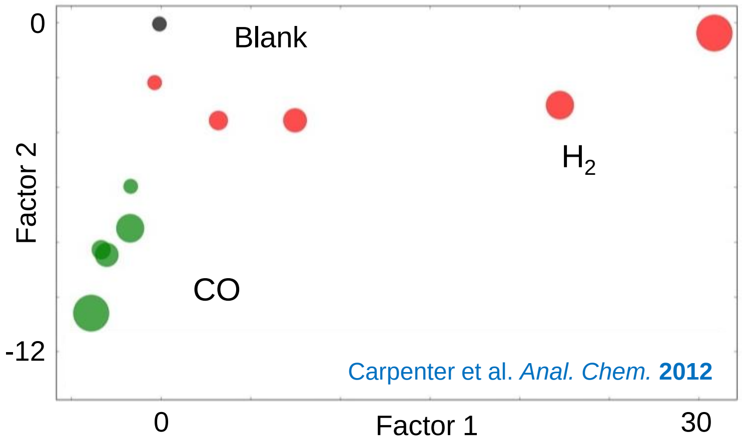

Potyrailo et al. *Nature Photonics* **2007**

Potyrailo et al., *Proc. Natl. Acad. Sci. U.S.A.* **2013**

Potyrailo et al. *Nature Communications* **2015**

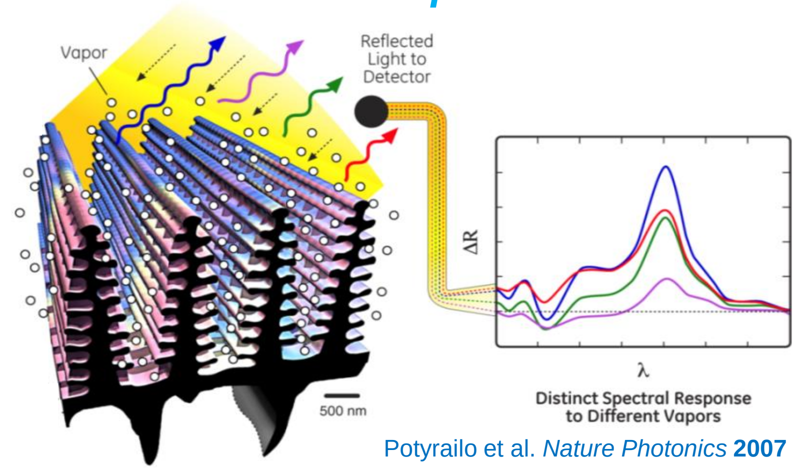
# Previous results for multivariable optical sensors

## High temperature sensing materials with diverse gas response mechanisms



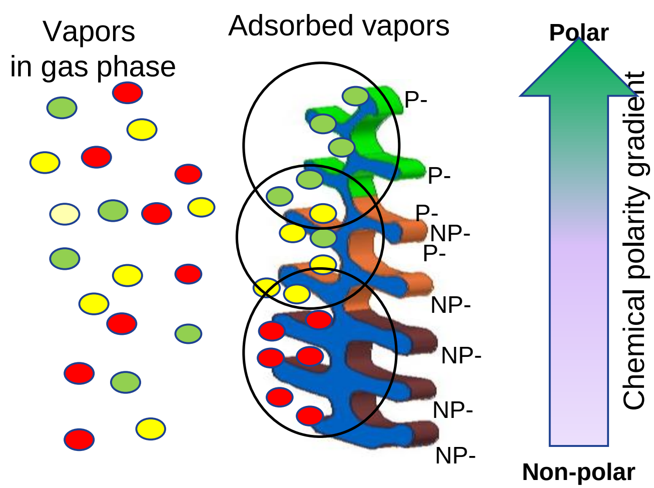

Carpenter et al. *Anal. Chem.* **2012**

## Unusually high vapor response selectivity of natural *Morpho* scales



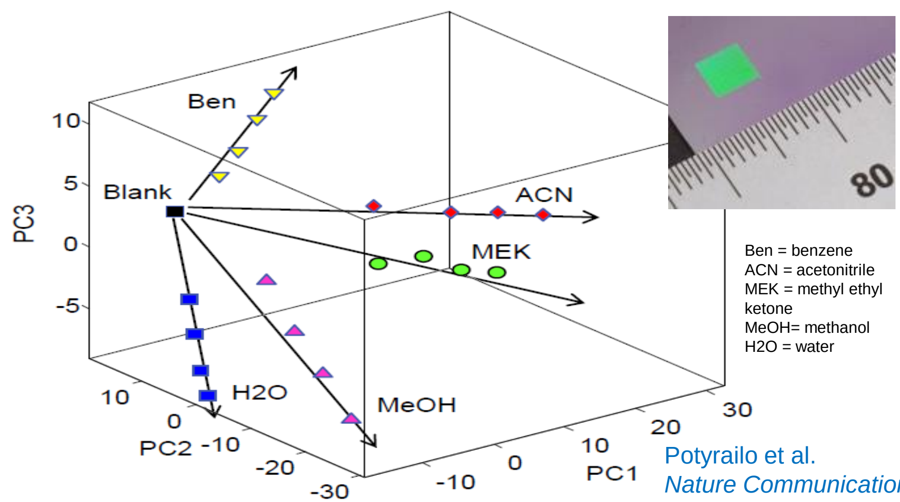

Potyrailo et al. *Nature Photonics* **2007**

## Understanding of origin of selective vapor response




Potyrailo et al. *Proc. Natl. Acad. Sci. USA* **2013**

## Design rules for bio-inspired highly selective gas sensors

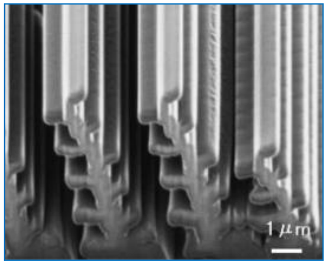



Ben = benzene
ACN = acetonitrile
MEK = methyl ethyl ketone
MeOH= methanol
H2O = water

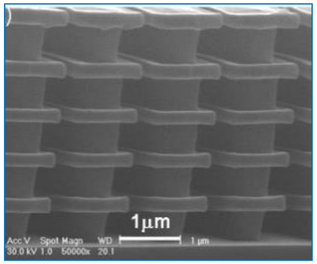
Potyrailo et al. *Nature Communications* **2015**

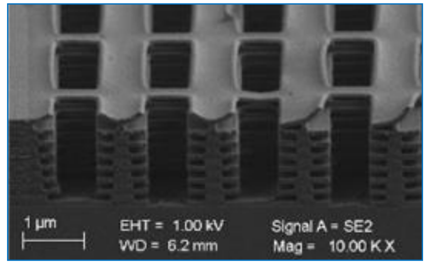
# Diversity of fabricated bio-inspired nanostructures

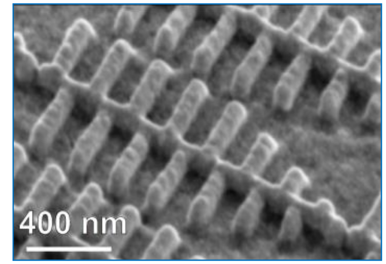
FIB CVD

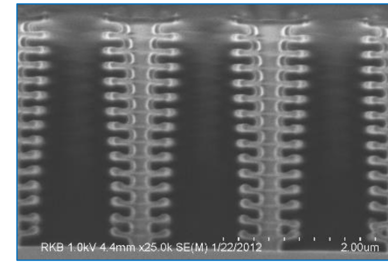



Electron-beam lithography

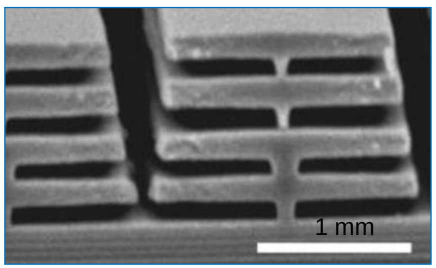


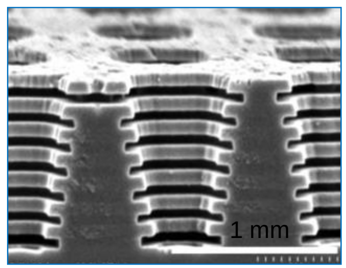



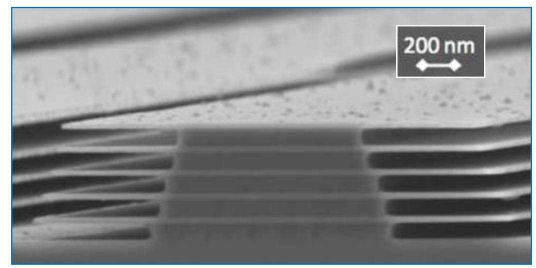




CVD, UV litho, chemical etching

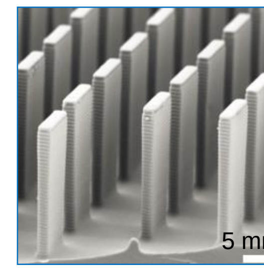


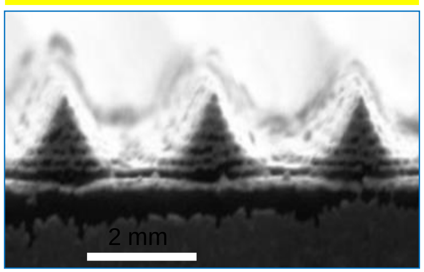

Selective etching of ALD material



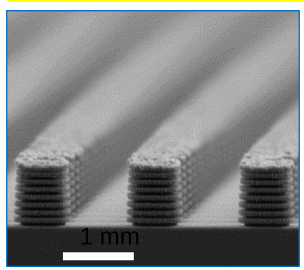

Double-molding

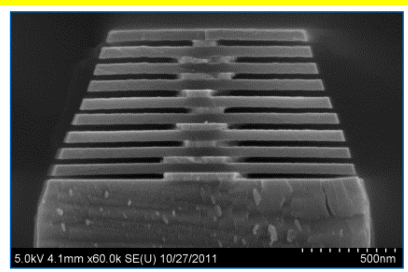


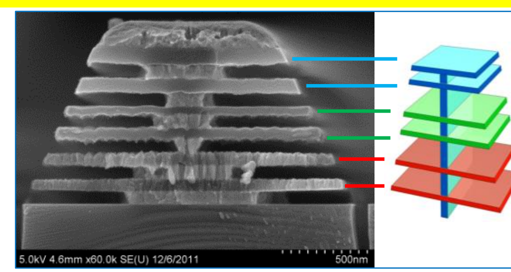

laser interference litho




Conventional photolithography and chemical etching



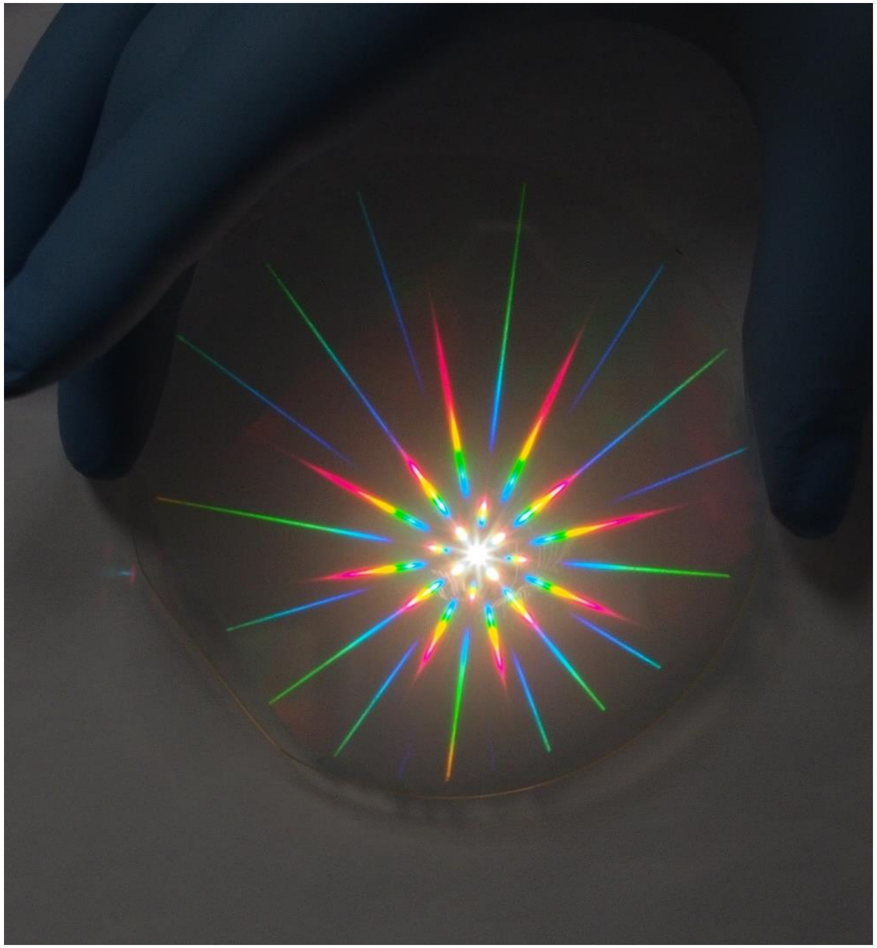



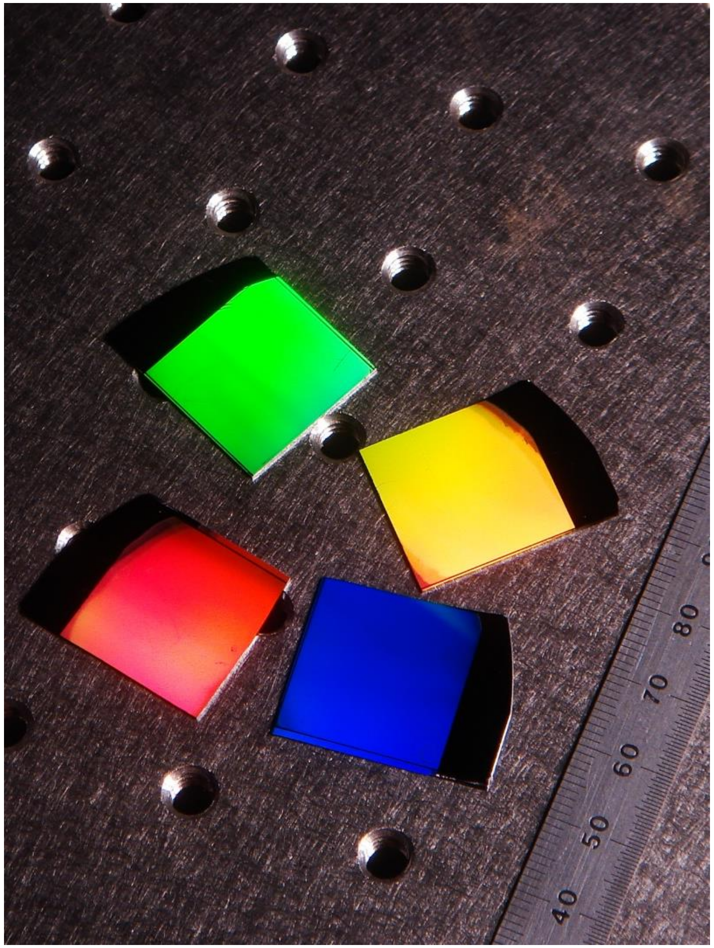




R. Potyrailo, *Chem. Rev*. **2016**

FIB CVD = Focused ion-beam
CVD = chemical vapor deposition
ALD = atomic layer deposition

# Examples of 3D sensing materials utilized in this program

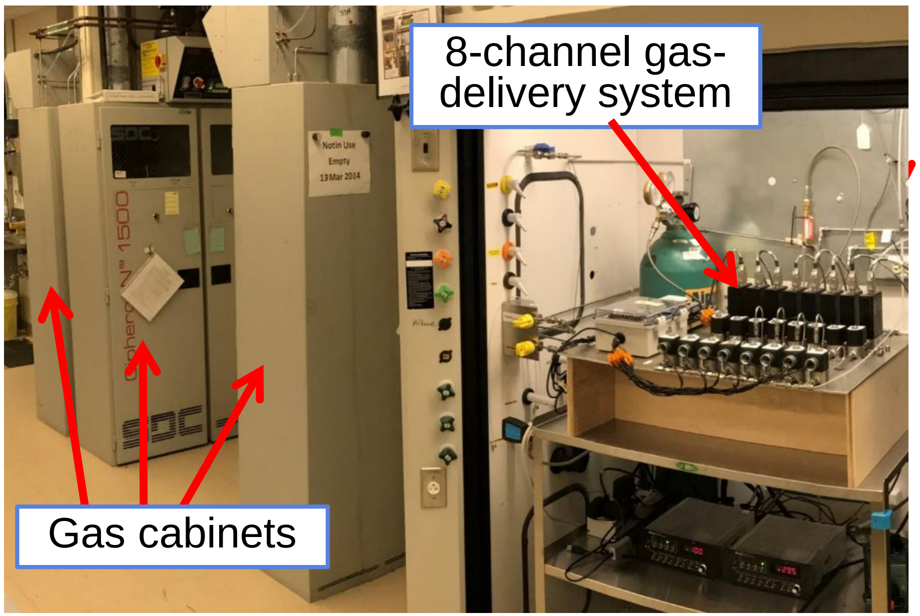




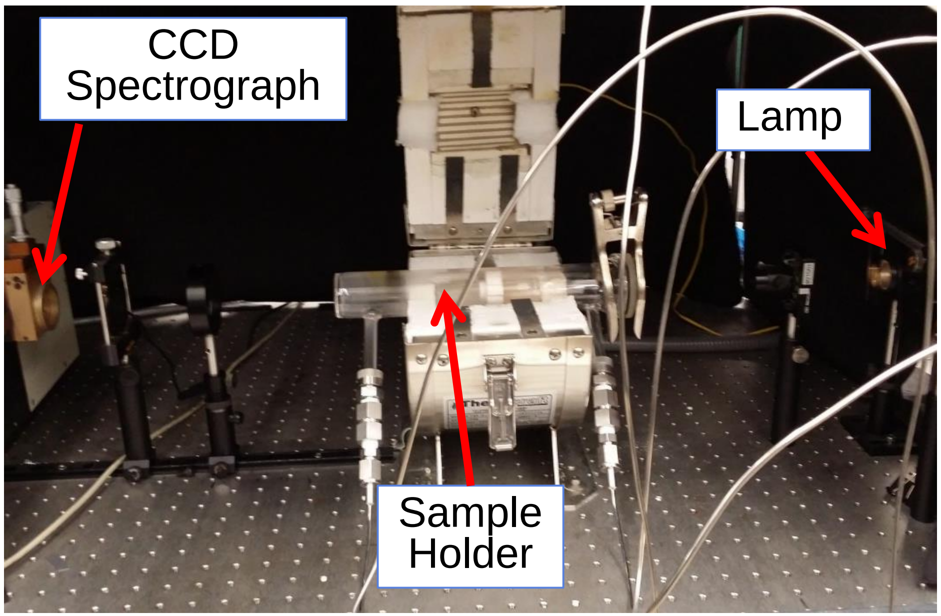
Innovative design of sensing structures for high selectivity gas detection

# In-house built multi-channel vapor generation and mixing systems

## Spectroscopy system

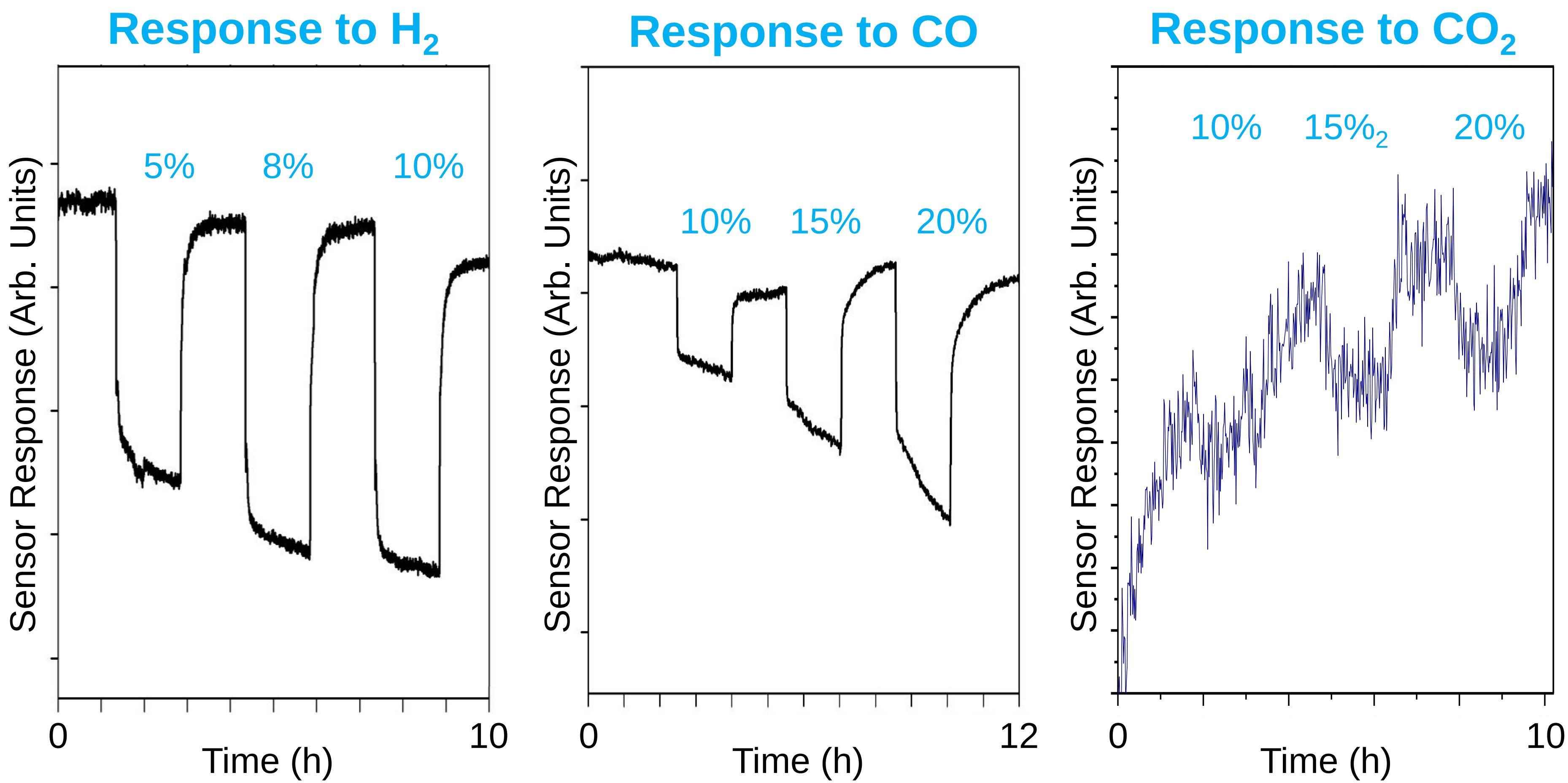



## Spectral imaging system




- Computer control
- Flexible flow profiles
- Multi-gas mixing

# Example of single-gas responses




On track for needed response sensitivity and speed

# Tools for data analysis of multivariable sensors:
## machine learning, data analytics, multivariate statistics

### Supervised learning
Artificial neural network
Bayesian statistics
Case-based reasoning
Gaussian process regression
Gene expression programming
Group method of data handling
Inductive logic programming
Instance-based learning
Lazy learning
Learning Automata
Learning Vector Quantization
Logistic Model Tree
Minimum message length
Probably approximately correct learning
Random Forests
Support vector machines
Symbolic machine learning

### Unsupervised learning
Expectation-maximization algorithm
Vector Quantization
Generative topographic map
Information bottleneck method
Self-organizing map
Association rule learning
Hierarchical clustering
Single-linkage clustering
Conceptual clustering
Cluster analysis
K-means algorithm
Fuzzy clustering

### Semi-supervised learning
Generative models
Low-density separation
Graph-based methods
Co-training

### Reinforcement learning
Temporal difference learning
Q-learning
Learning Automata

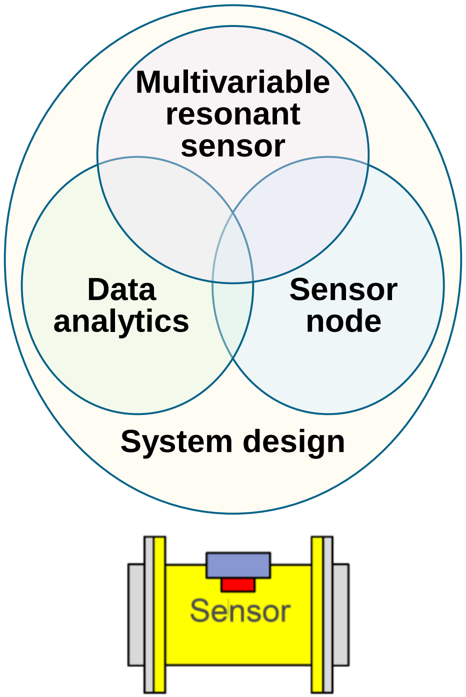
### Deep learning
Deep belief networks
Deep Boltzmann machines
Deep Convolutional neural networks
Deep Recurrent neural networks
Hierarchical temporal memory

Wikipedia.org

**Increasing role of data analytics in high performance sensing**

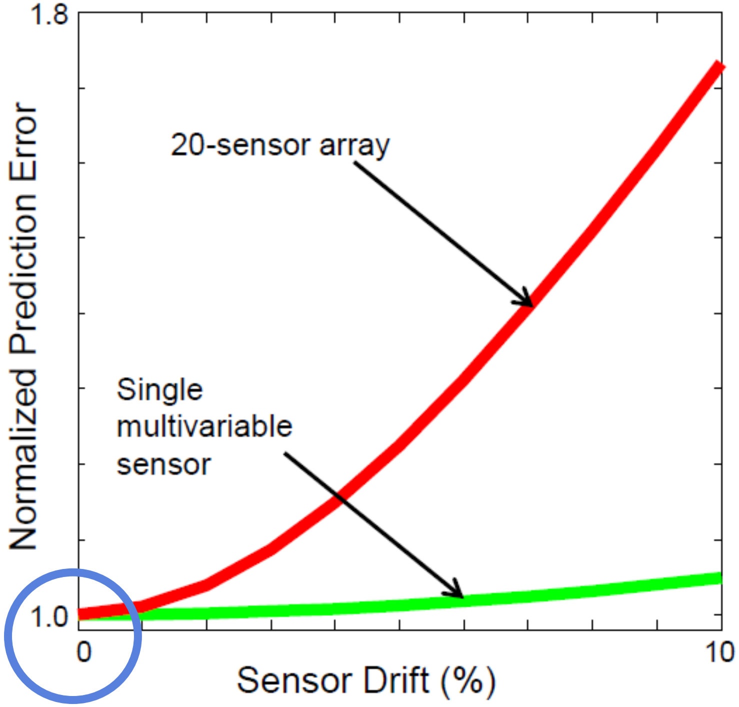
# Toward selective and stable bio-inspired gas sensors for solid oxide fuel cells

## System concept



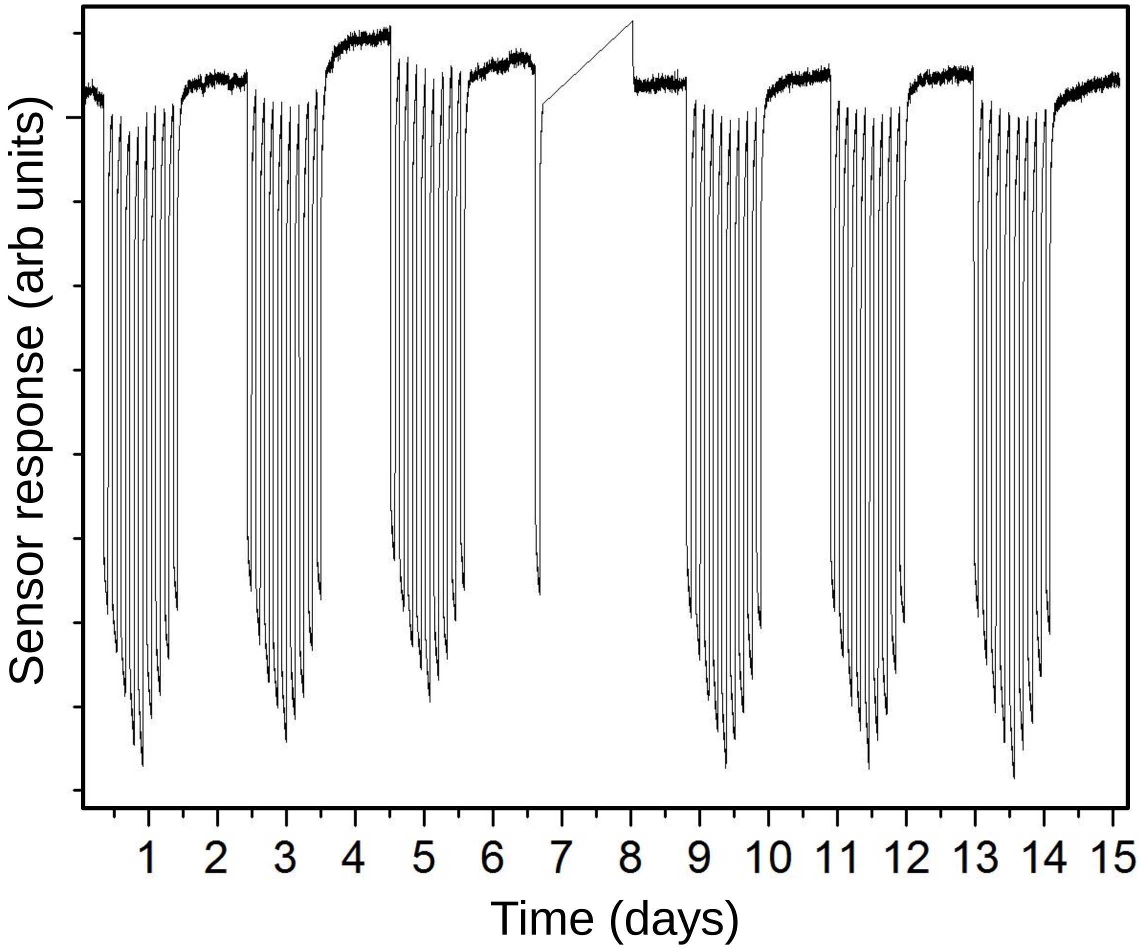

## Field test

## Stability of multivariable sensor



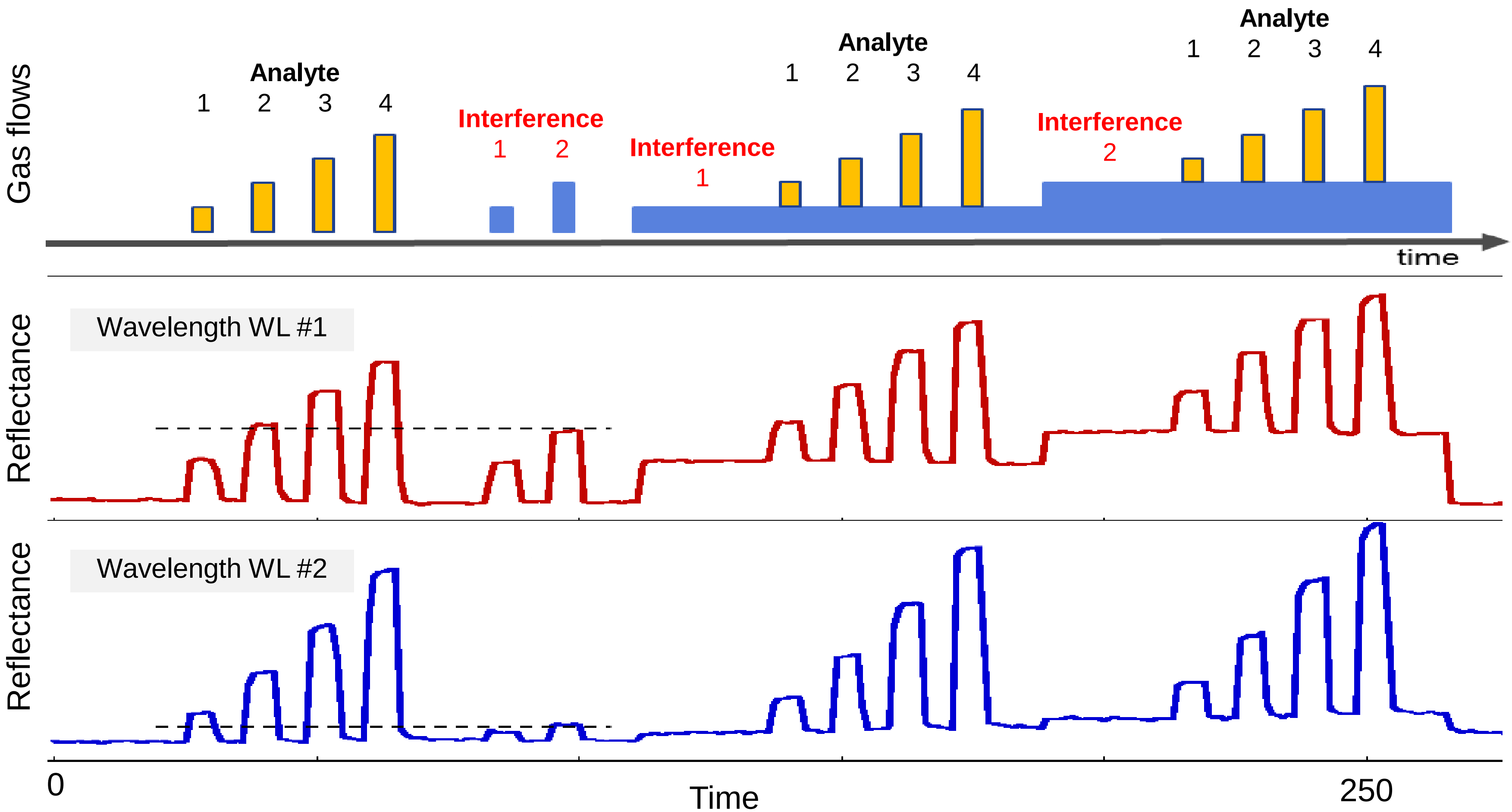
# Initial response stability

## Example: $H_2$ gas



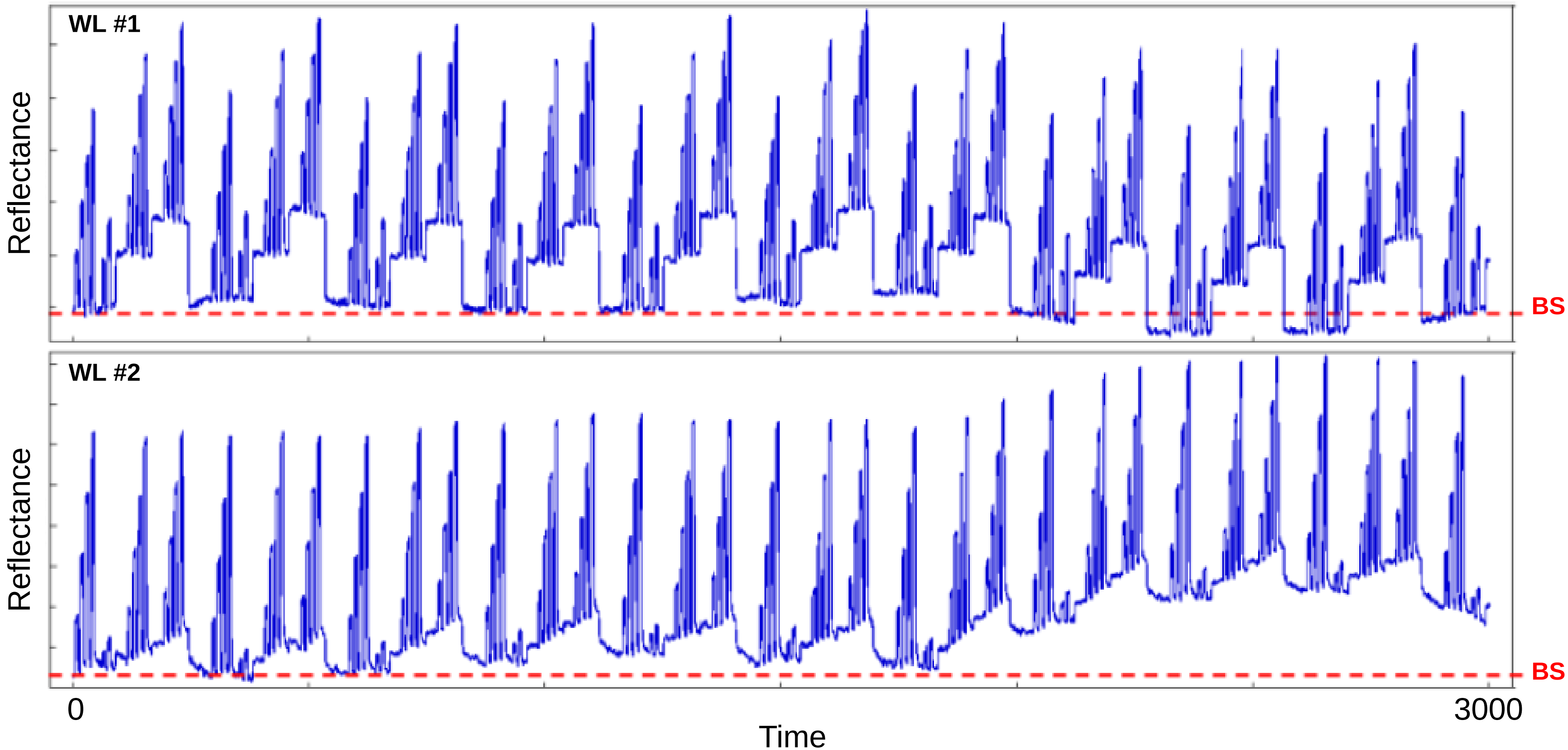

Baseline studies of sensor stability

# Short-term responses of sensor:
## analyte, interference, their mixtures




Excellent short term response for selective analyte quantitation

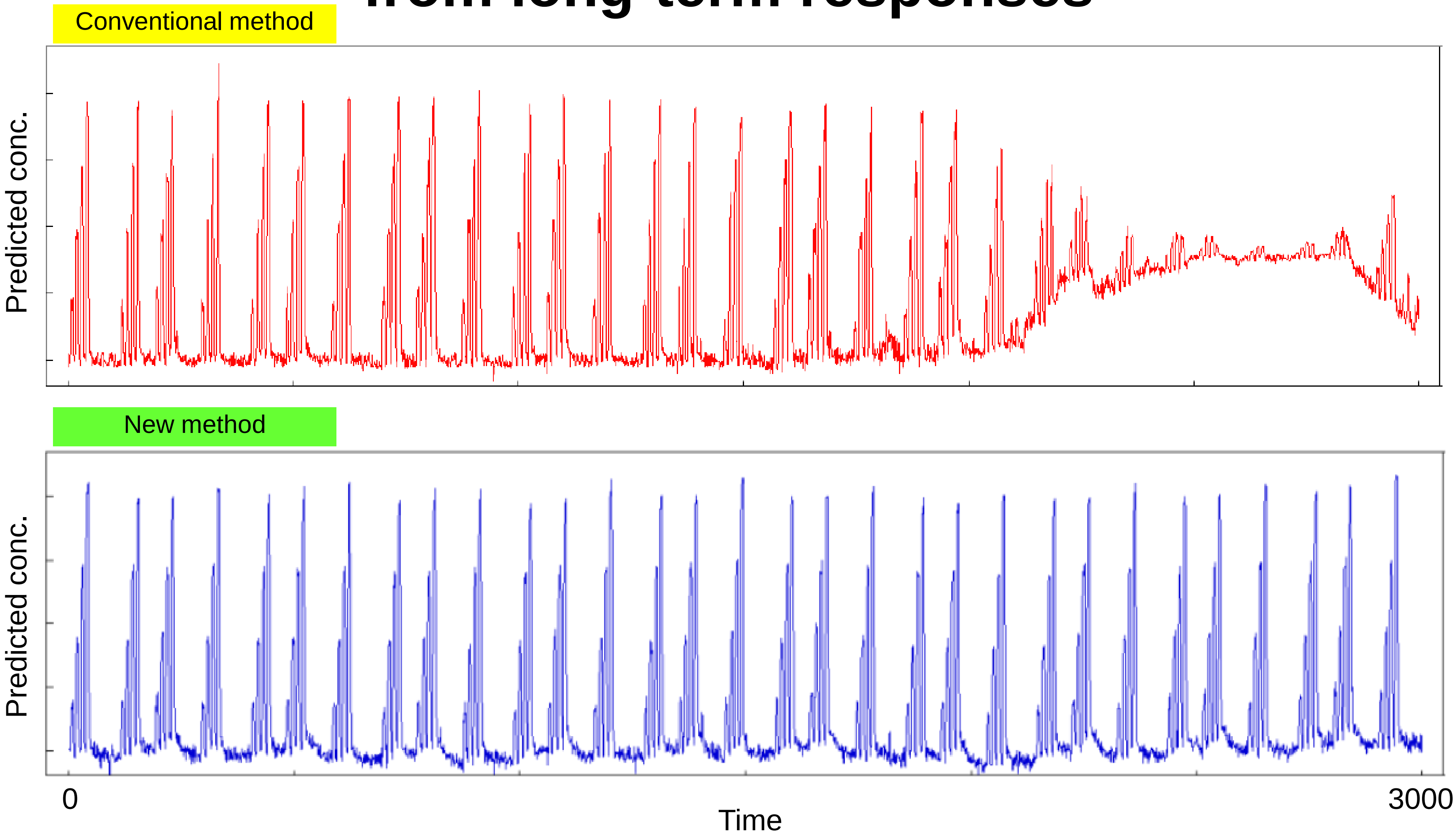
# Long-term responses of sensing nanostructure:
## analyte, interference, their mixtures




Long term response exhibits strong baseline drift

WL = wavelength
BS = baseline

# Predicted analyte concentrations from long-term responses

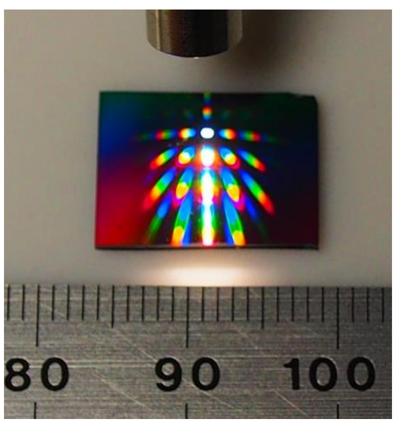



Corrected long term sensor baseline drift

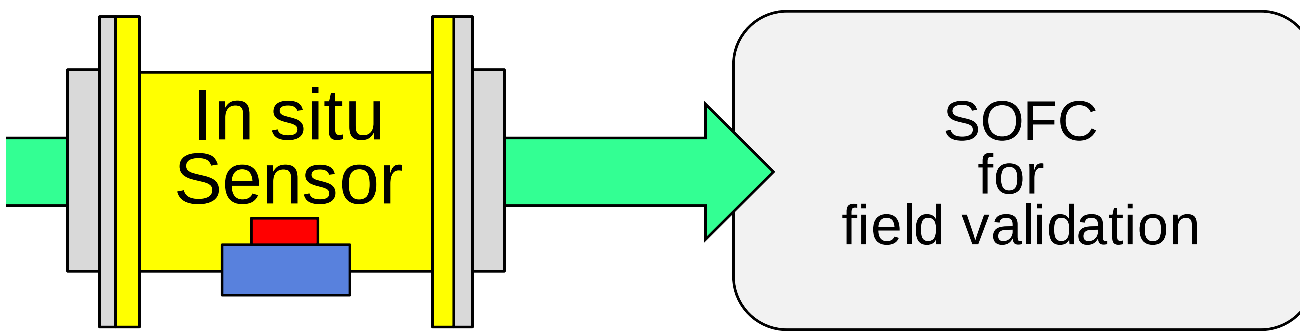
# Summary

- Design of bio-inspired sensing materials for simultaneous quantitation of several gases
- Refined material-design rules to operate at elevated temperatures
- Advancing fundamental understanding of multivariable gas sensors at high temperatures
- Initial stability tests started

**Current work**




**Upcoming work**



# Acknowledgements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- SUNY Albany team
- Steven Markovich @ DOE/NETL

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