Nano-electronic Nose and Proton-transfer Reaction Mass Spectrometry: A fruitful Synergy for Food Quality

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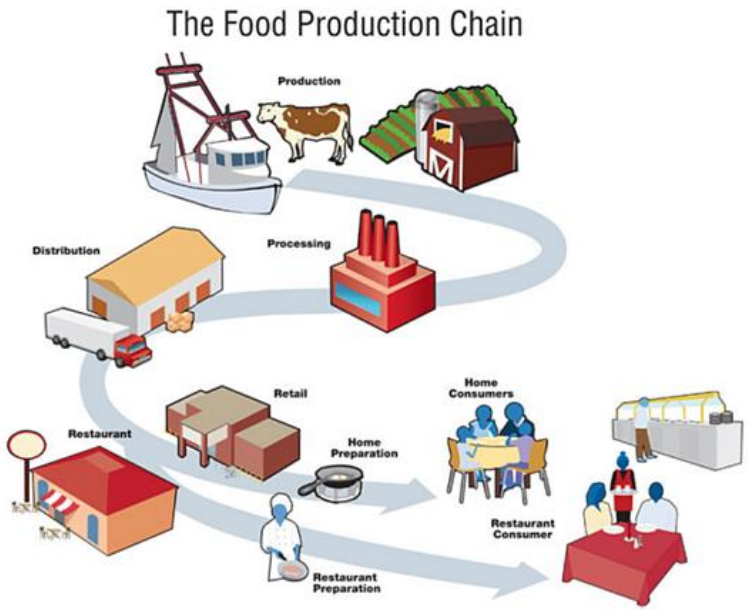
Outline

- Motivation
- Our approach (thermal gradient)
- Two declinations (time and space)
- Application to food quality
- Synergy with mass spectrometry

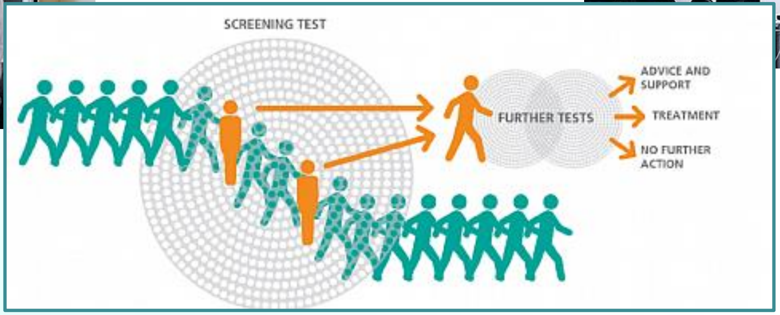
Food quality assessment

scientific instrumentation

panelists



doctors



Preventive screening

Tiny ~~&~~ or smart gas sensors

Gas chromatography
Mass-spectrometry

Resistive sensors

Tiny

Cheap

Portable

Integrable

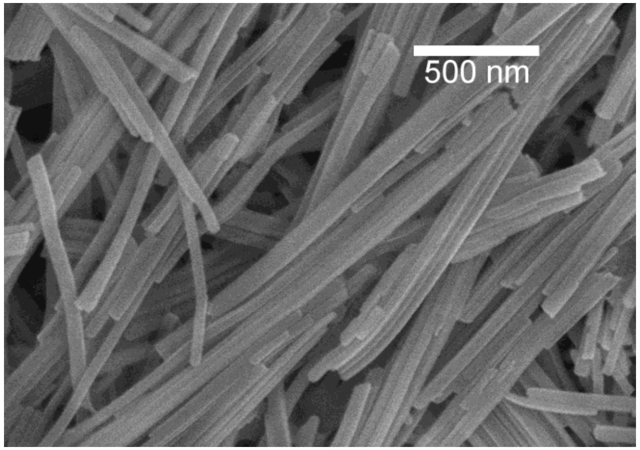
Sensitive

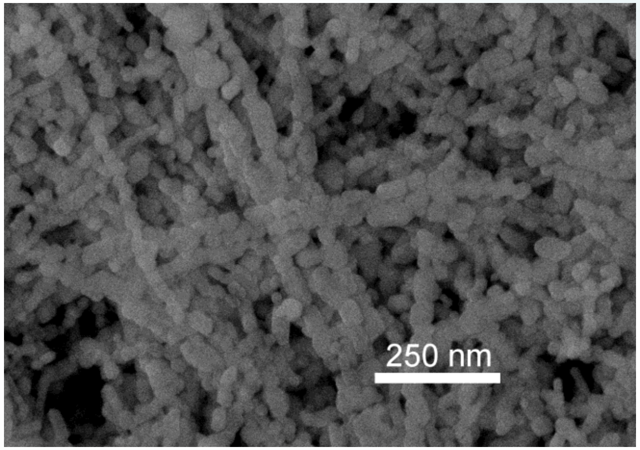
Recognizing

Multi-sensing

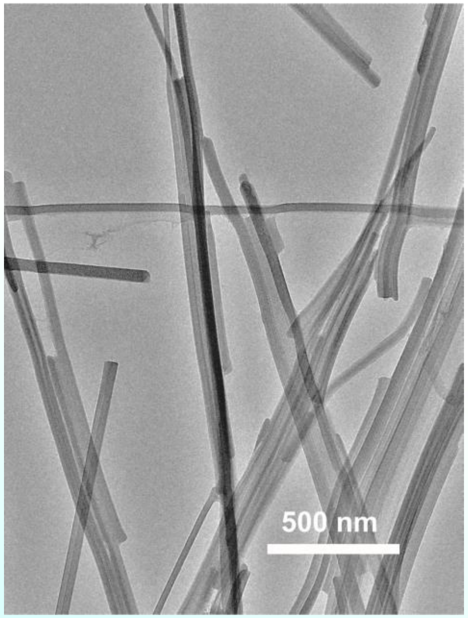
NiO nanowires: SEM, XRD, TEM

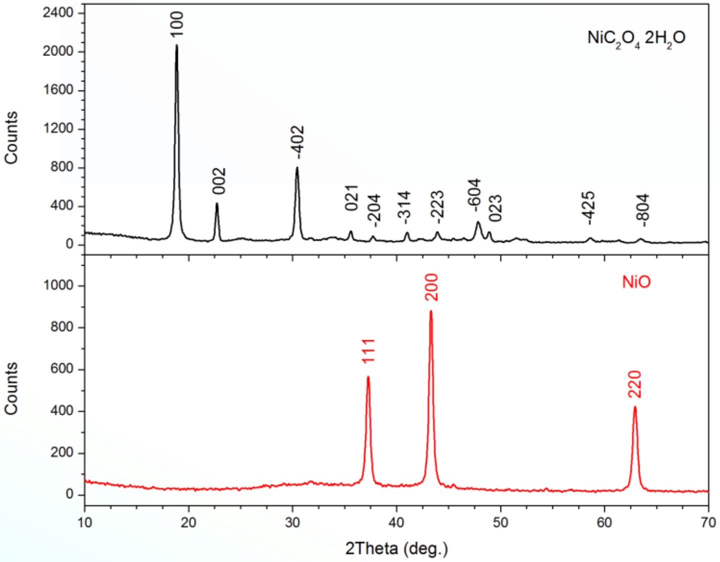
product 1

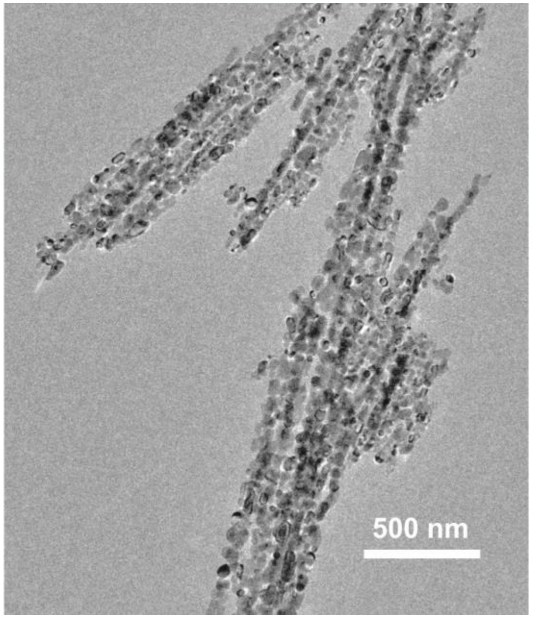




product 2

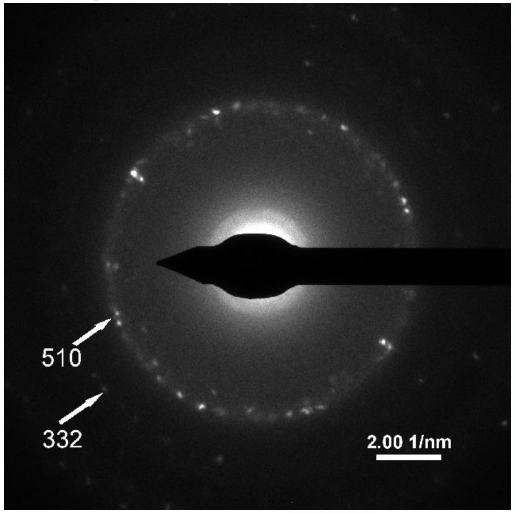


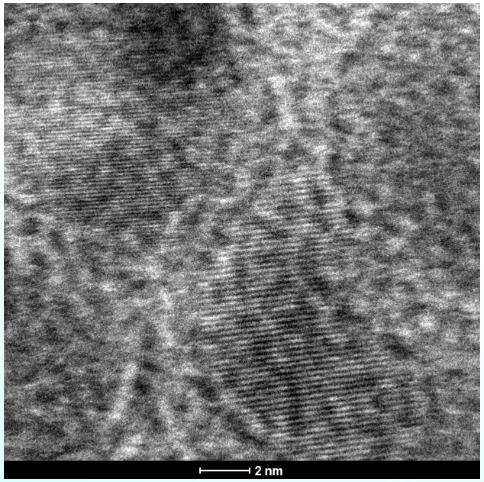




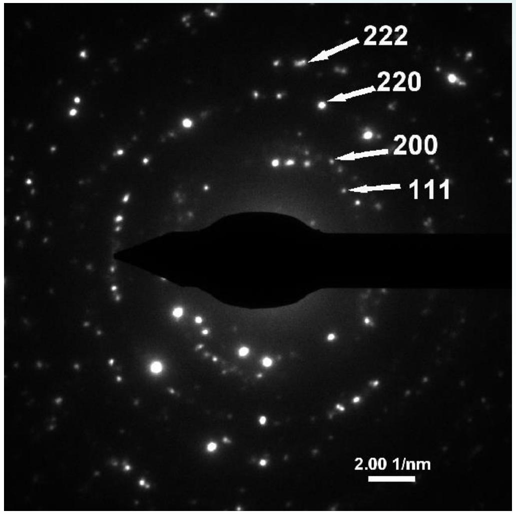
NiO nanowires: SAED, HRTEM

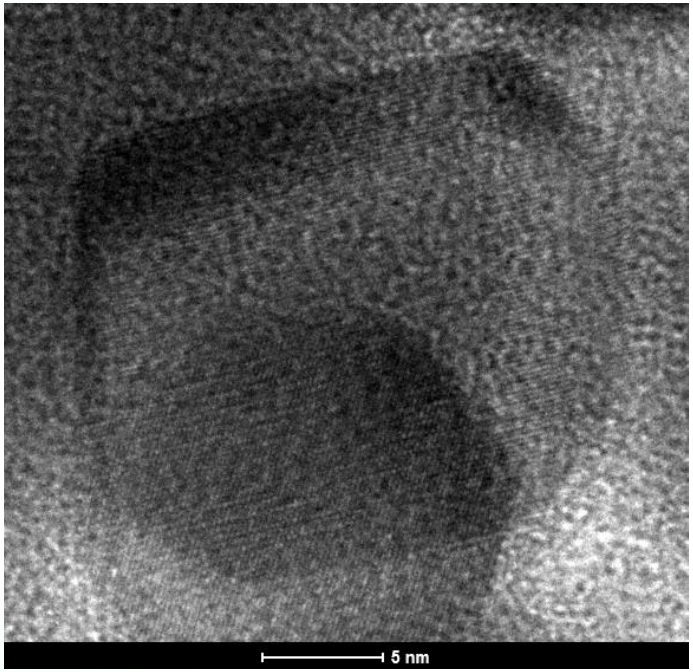
nickel oxalate hydrate





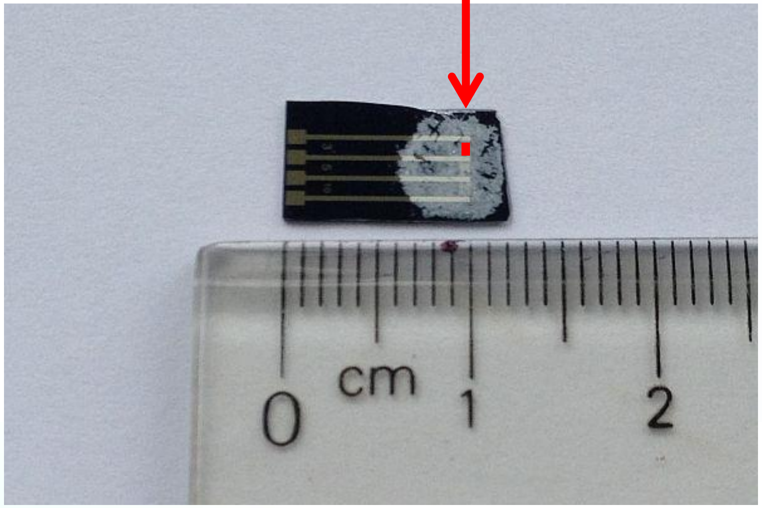
nickel oxide



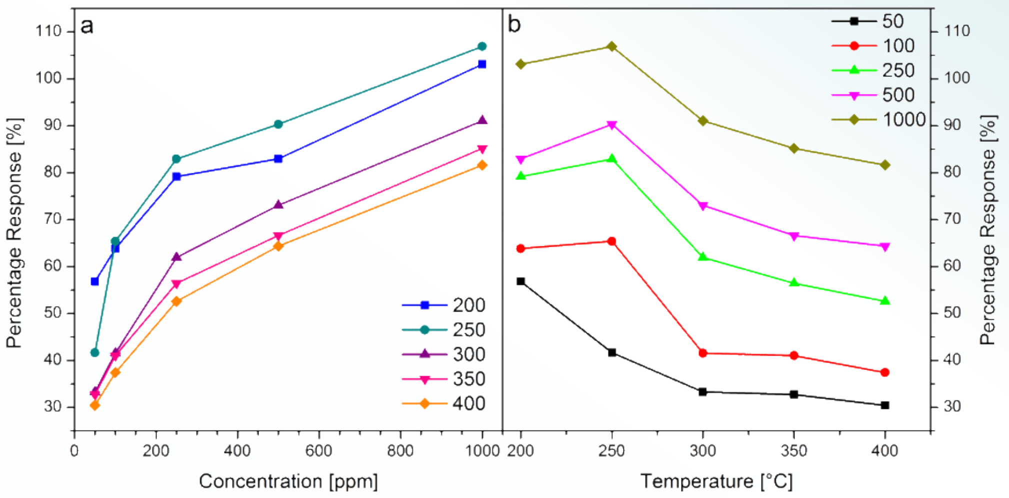


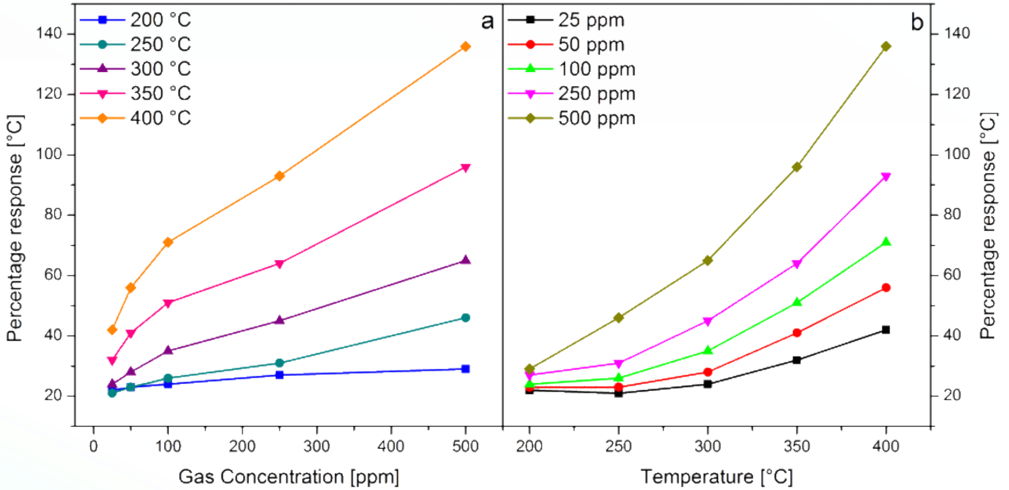
NiO NWs based sensor

Conductometric sensor



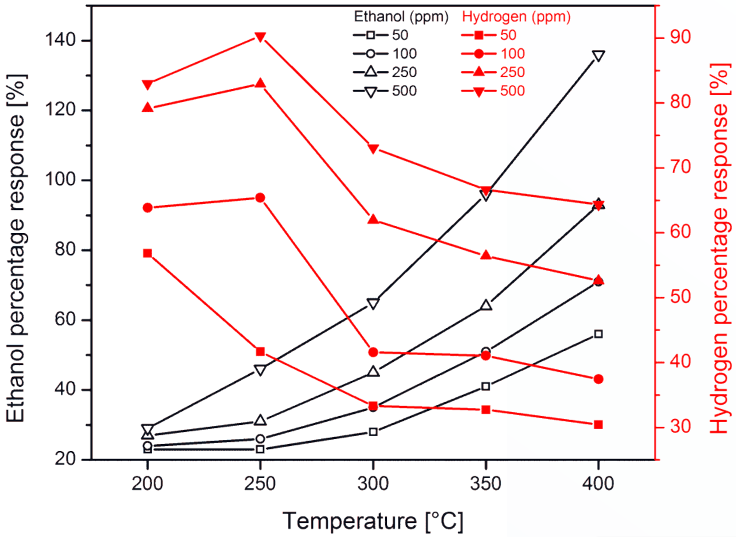
Hydrogen response



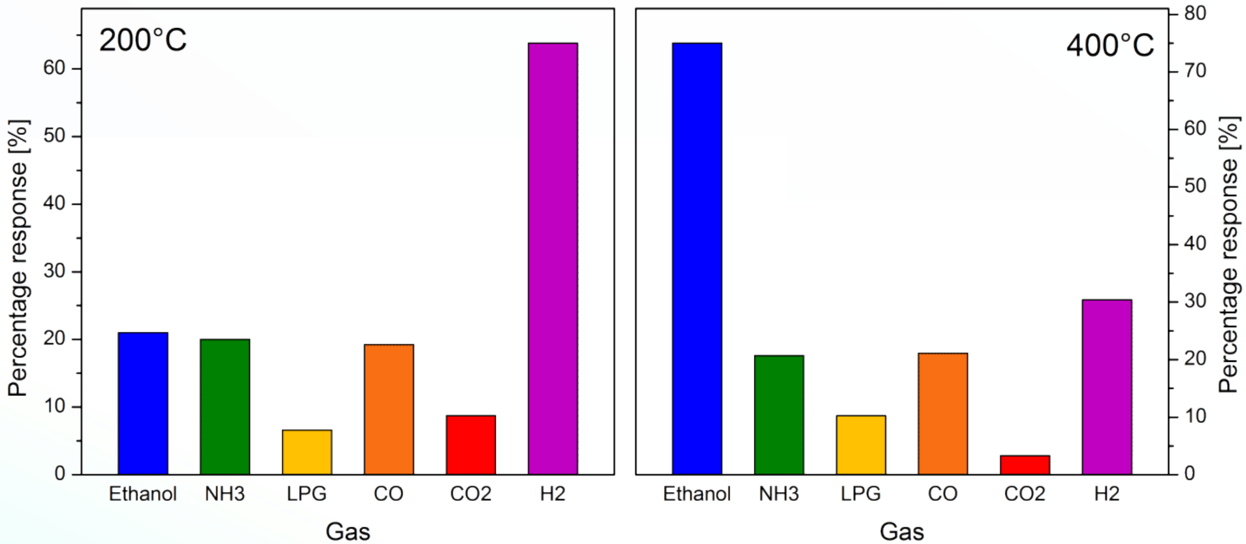


Ethanol response

Selectivity?



Conductometric sensor

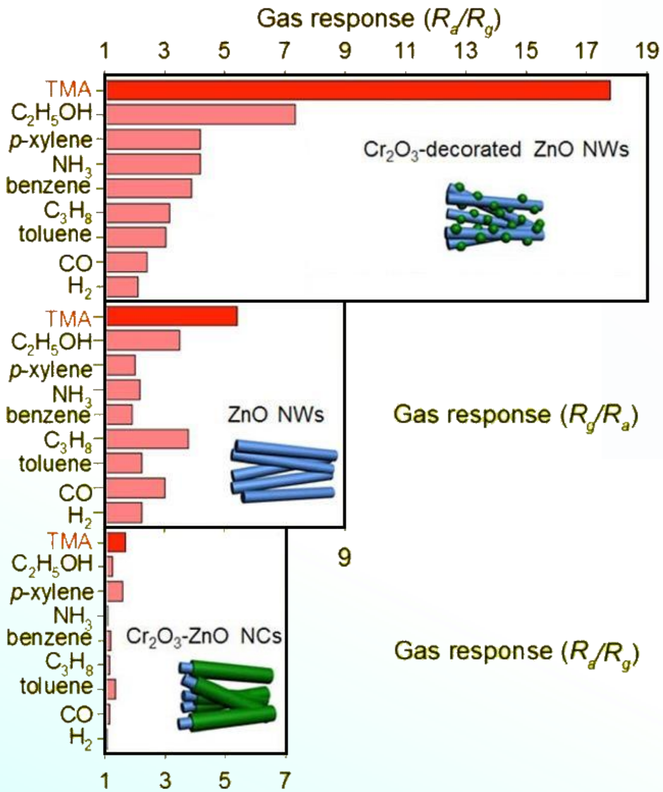


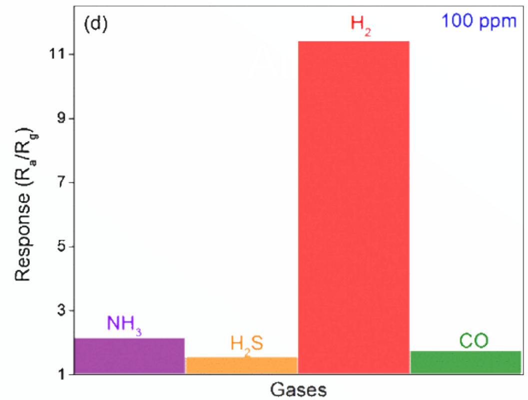
M. Tonezzer et al.,
Dual-selective hydrogen and ethanol sensor for steam reforming systems,
Sensors and Actuators B 236 (2016) 1011-1019.

Selectivity?

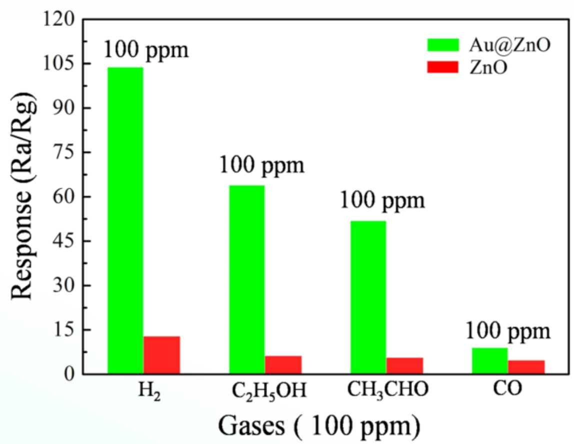
"selectivity" conductometric sensor

Highly sensitive and **selective** trimethylamine sensor using one-dimensional ZnO–Cr_2O_3 hetero-nanostructures, Nanotechnology 23 (2012) 245501.

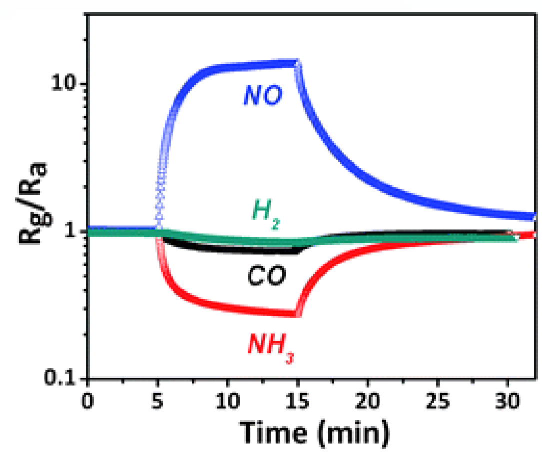




Highly sensitive and **selective** hydrogen gas sensor using sputtered grown Pd decorated MnO_2 nanowalls, Sensors & Actuators B 234 (2016) 8-14.

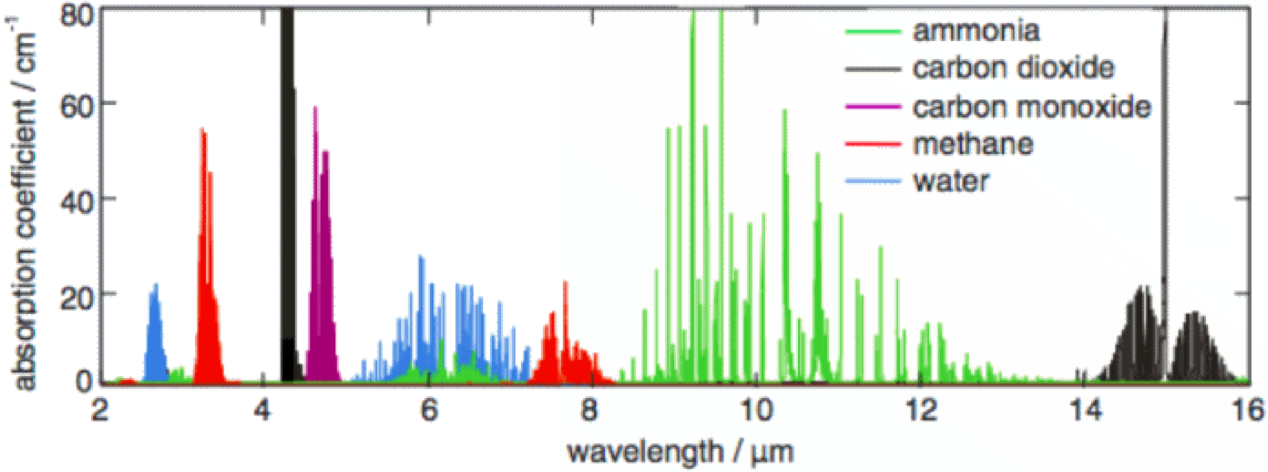


Facile Approach to Synthesize Au@ZnO Core–Shell Nanoparticles and Their Application for **Highly** Sensitive and **Selective** Gas Sensors, ACS Appl. Mater. Interfaces, 2015, 7, 9462–9468.

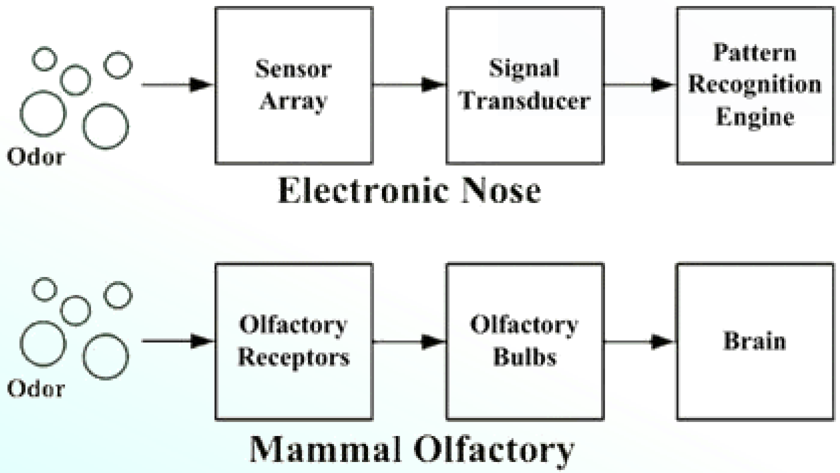


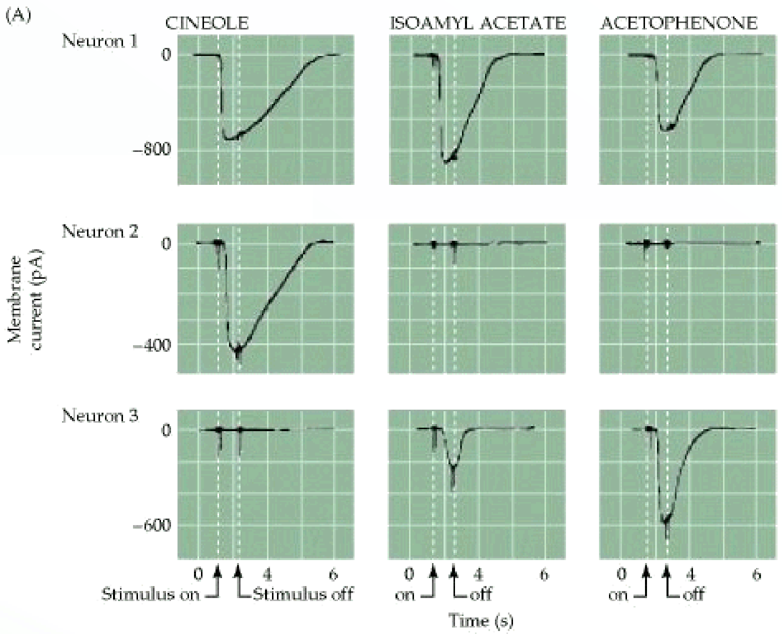
Optimization of a zinc oxide urchin-like structure for high-performance gas sensing, J. Mater. Chem. 2012, 22, 1127-1134.

Intrinsic vs Electronic Nose



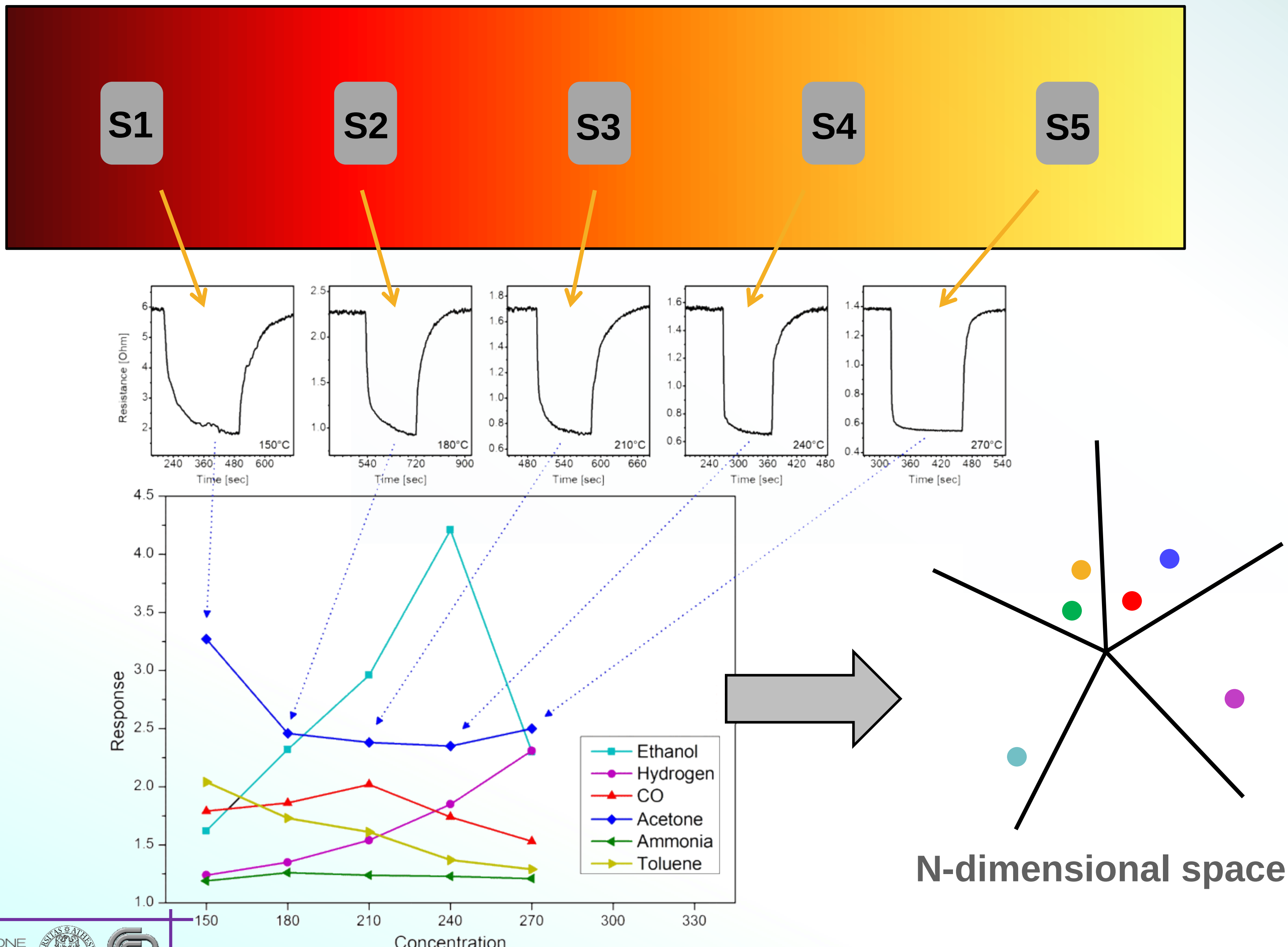
optical sensor





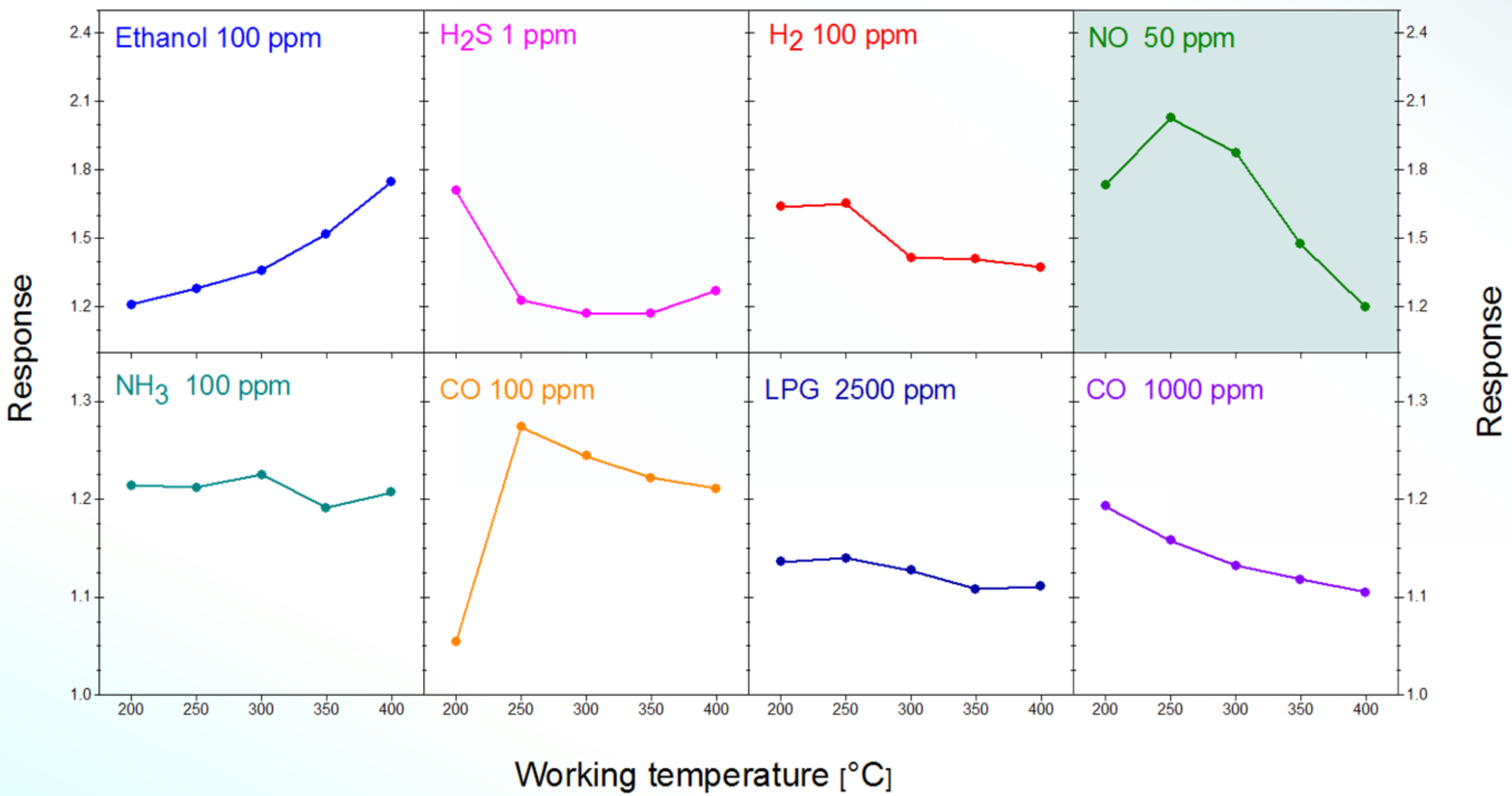
~1000 odoral receptors
(3% of genome)

Thermal gradient



Thermal fingerprints

intrinsic selectivity



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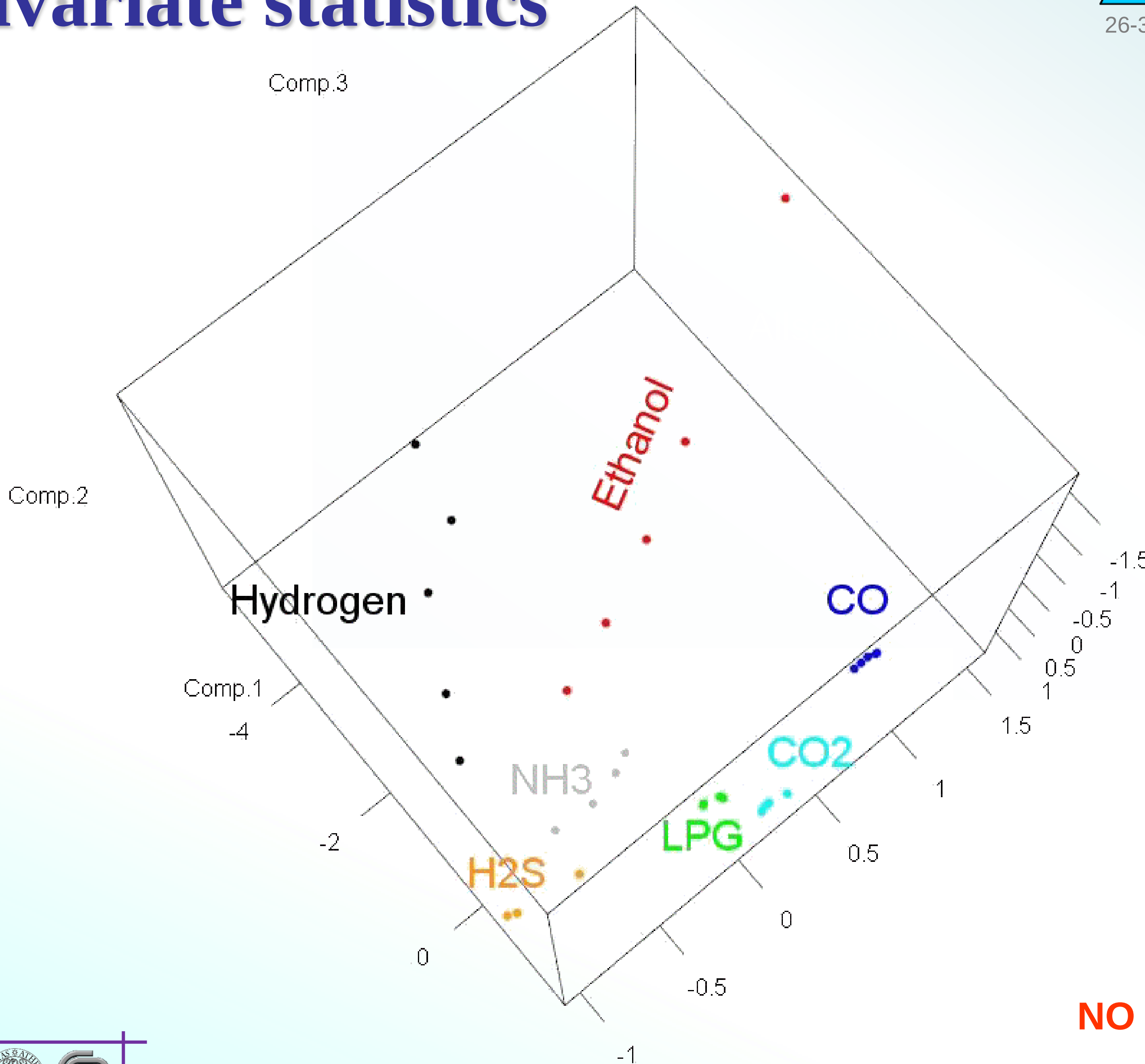
Multivariate statistics



NO HCA

Double-blind classification

support vector machine

random forest classification

	CO	CO_2	Ethanol	H_2	H_2S	LPG	NH_3
CO	8						
CO_2		7					
Ethanol			8				
H_2				8			
H_2S							
LPG							
NH_3							

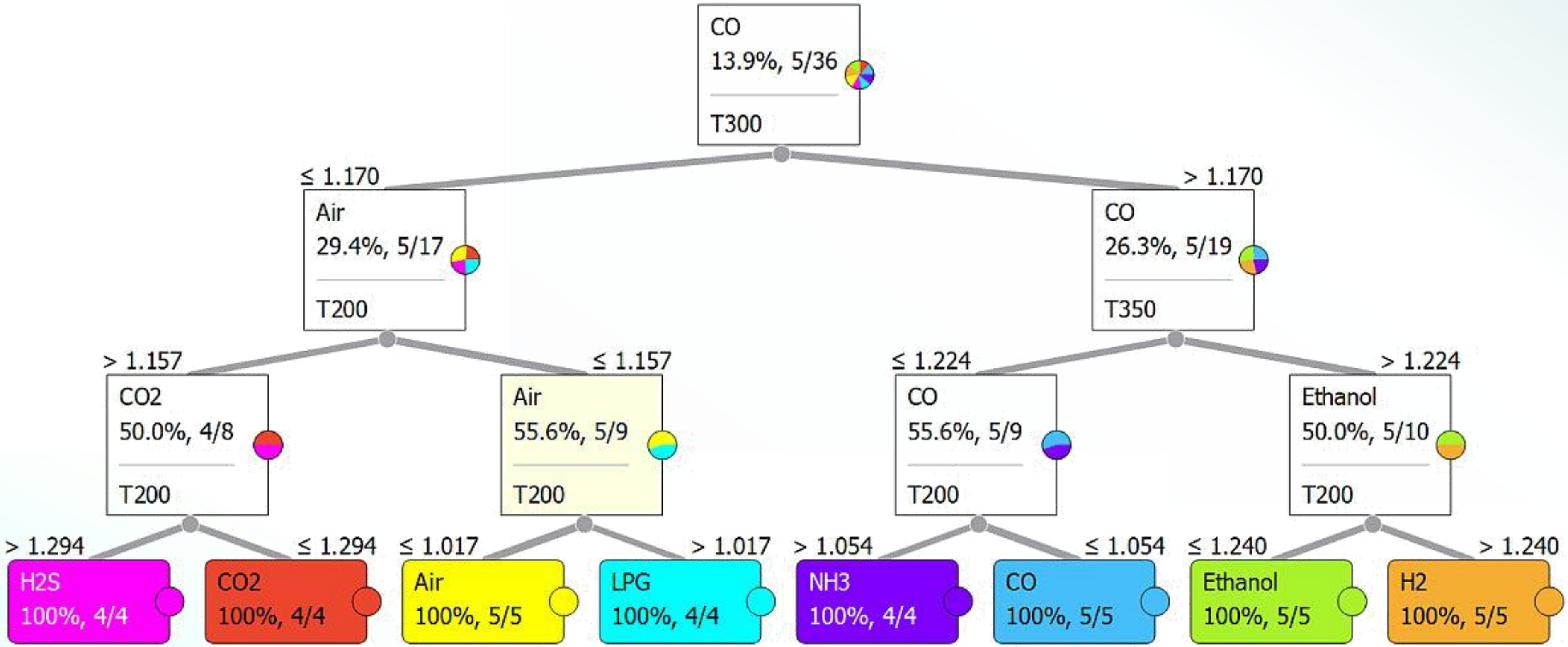
classification tree

logistic regression

classification…

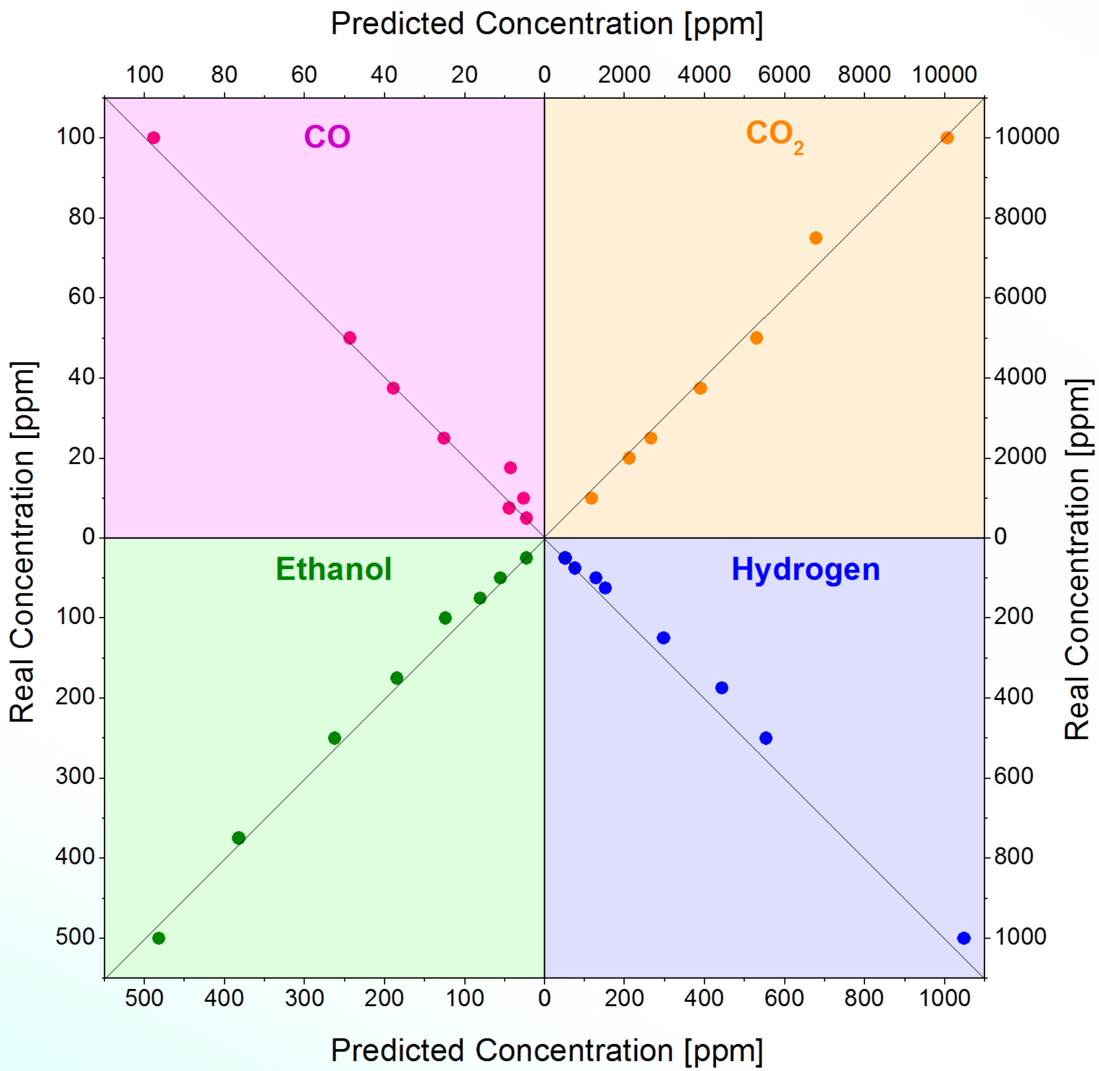
Double-blind classification

classification tree



classification… is it enough?

Quantitative estimate



**trained
linear regression**

RMSE

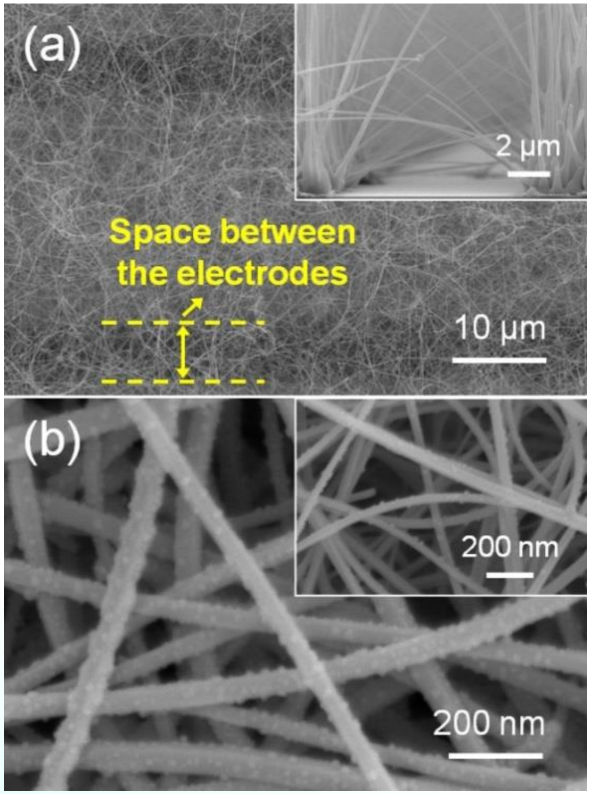
CO: 17%

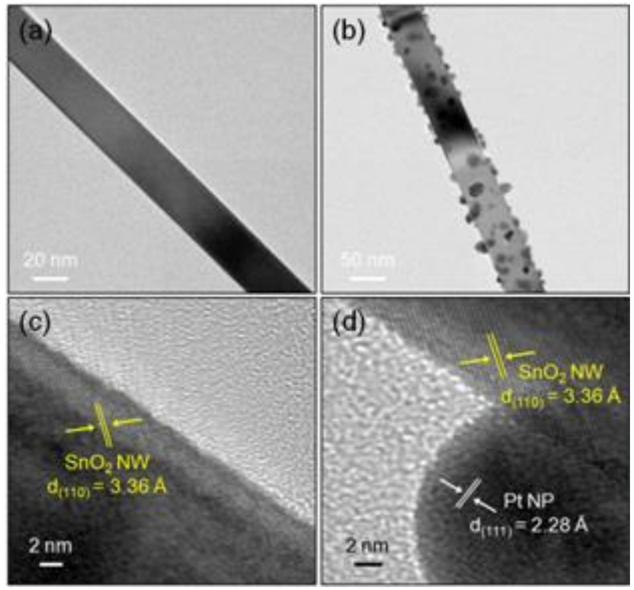
CO_2: 12%

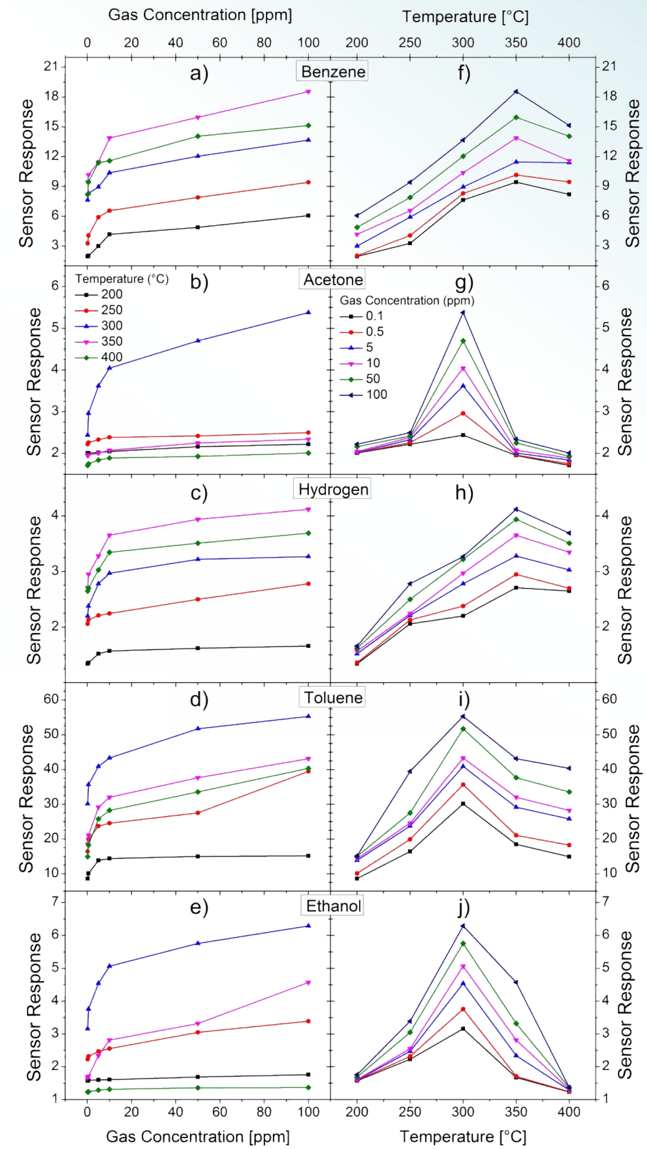
Ethanol: 16%

H_2: 14%

Pt-decorated SnO_2 nanowires

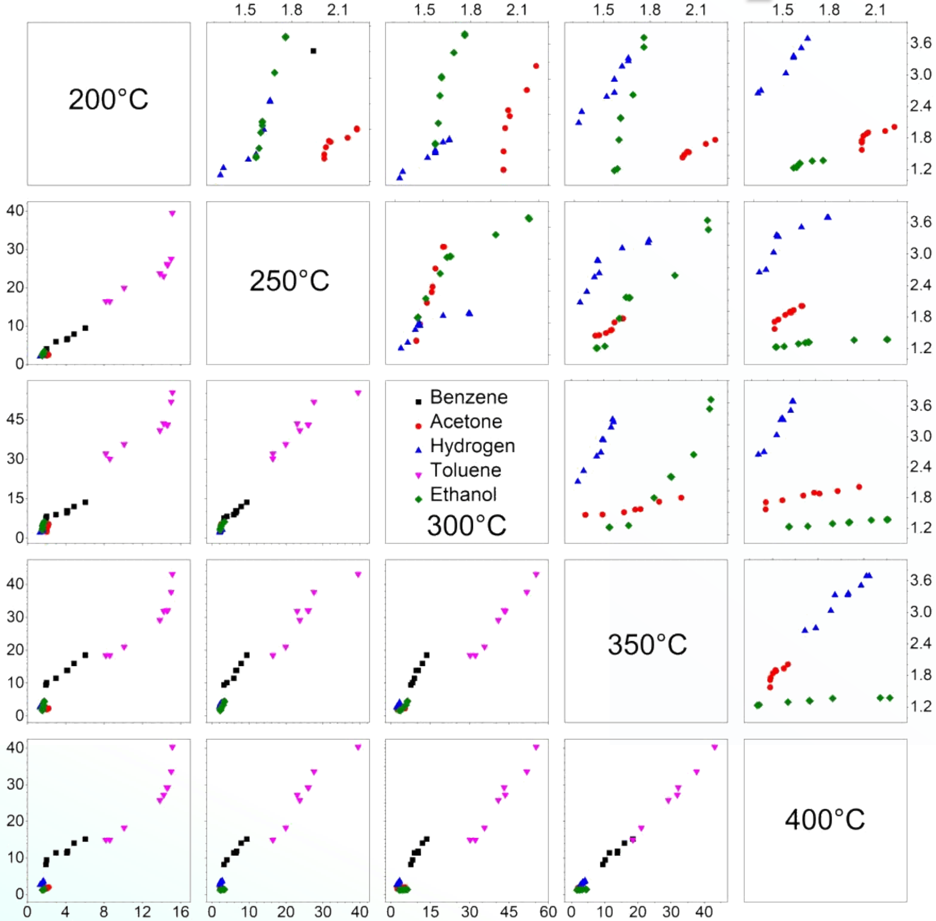


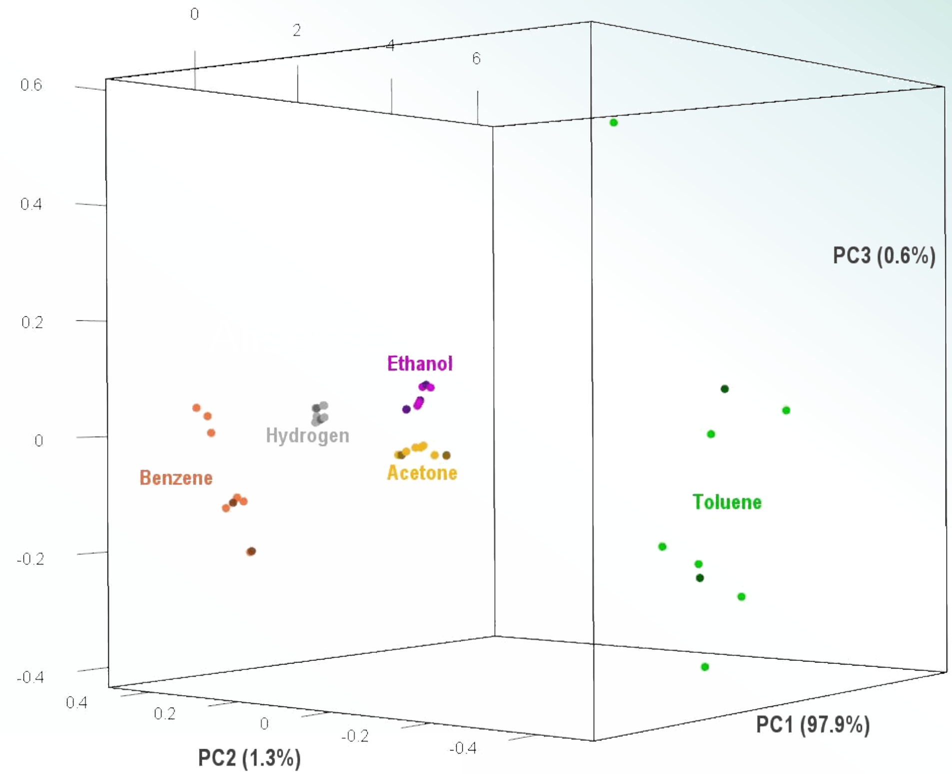


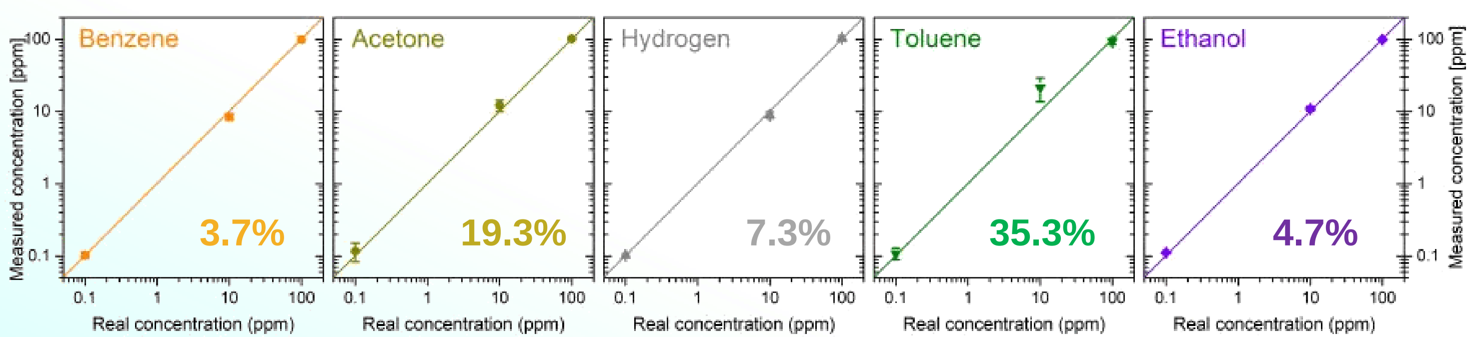


Prof. Sang Sub Kim
INHA University

Pt-decorated SnO_2 nanowires

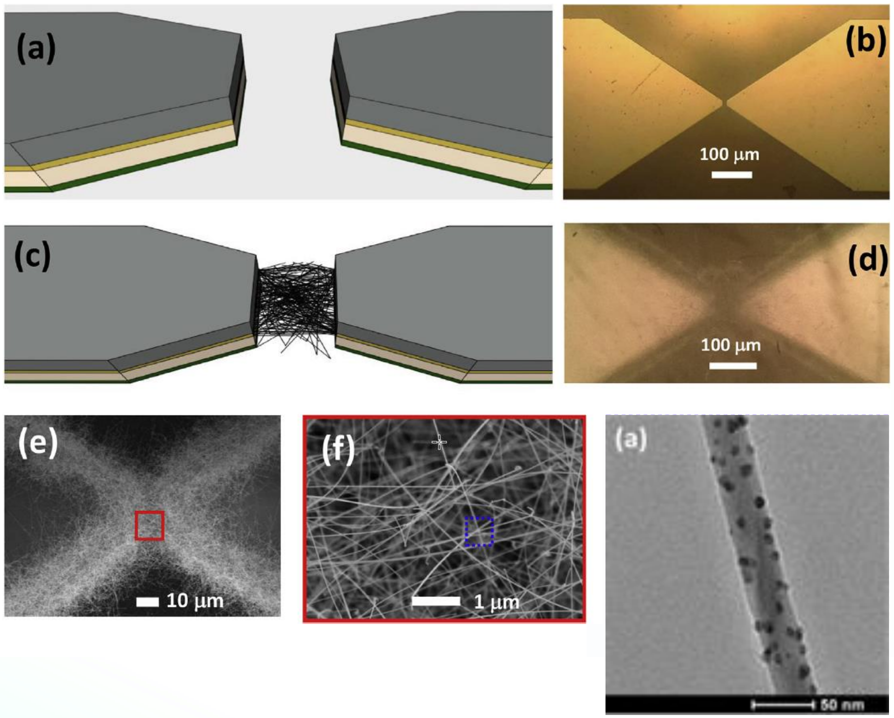


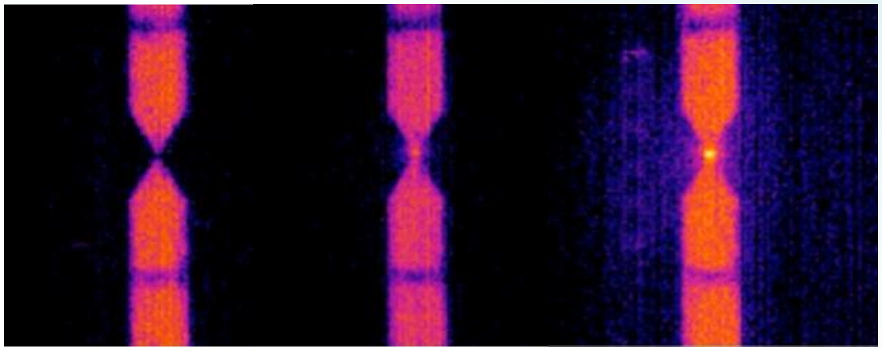




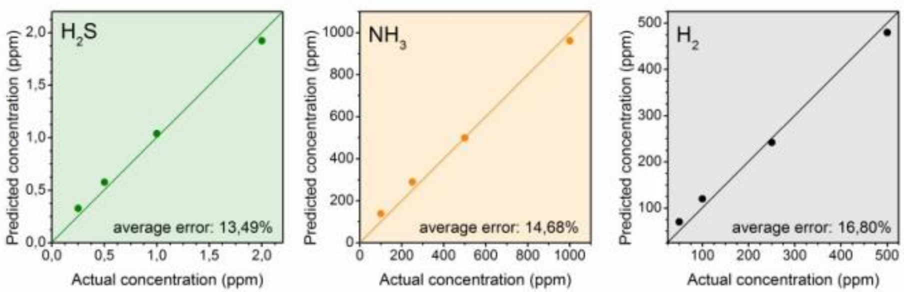
Temporal gradient

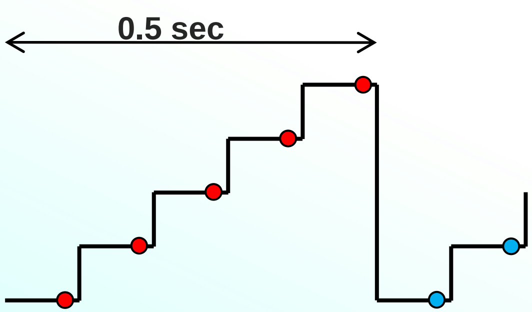
"sandwich-oriented" growth

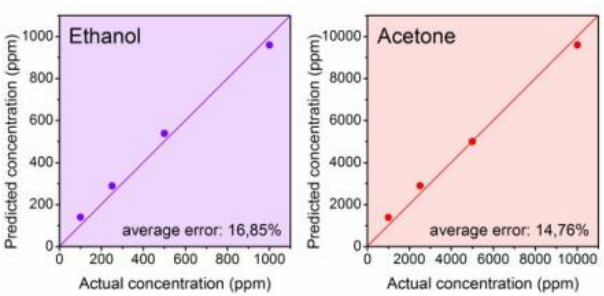




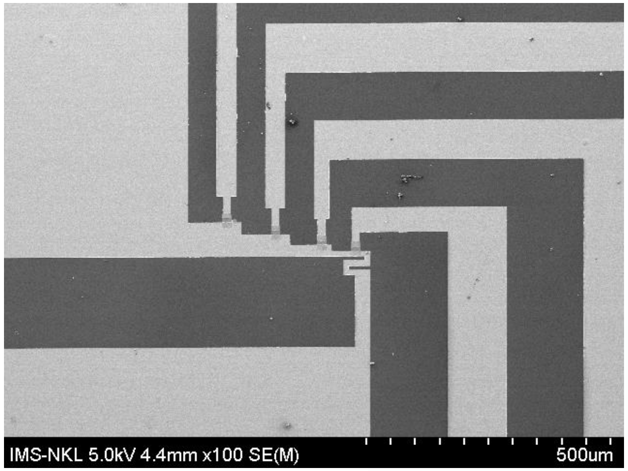
8mW 16mW 20mW

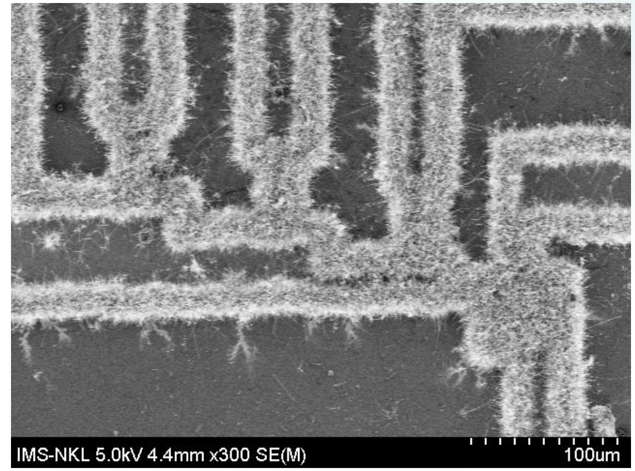




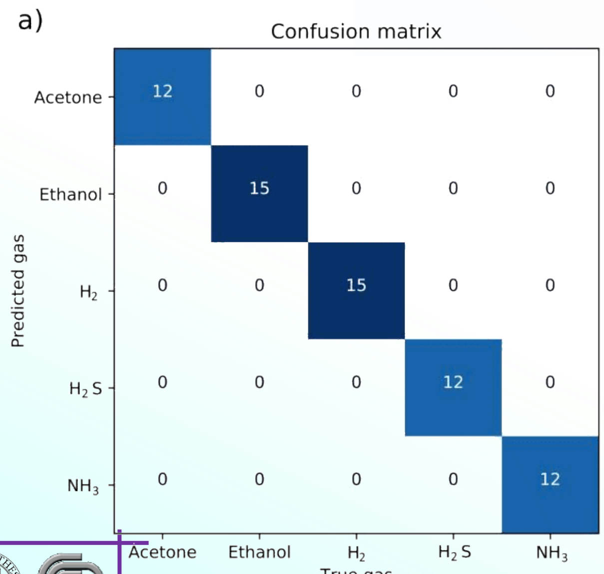


Spatial gradient

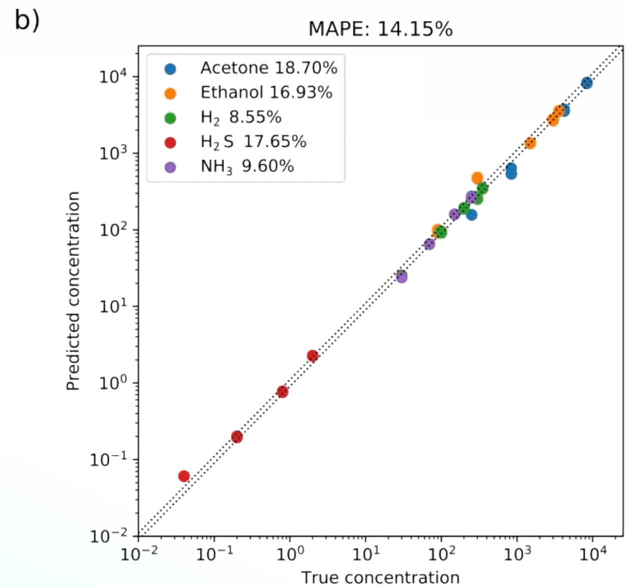




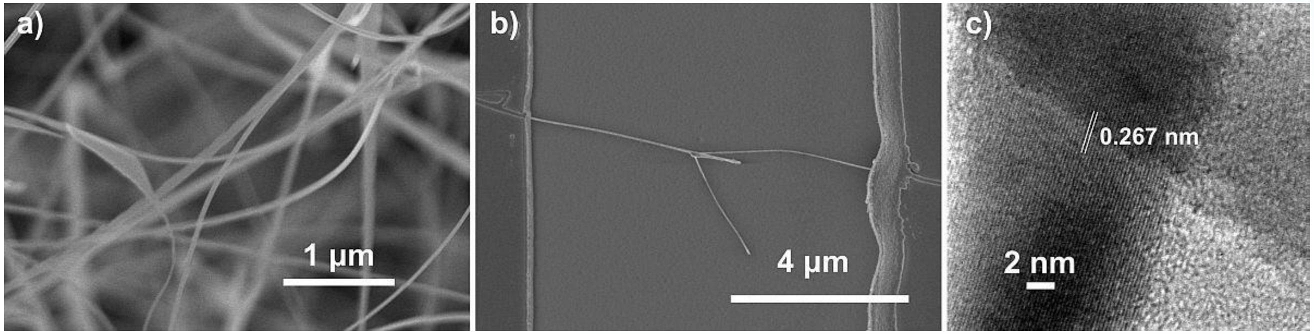
classification



quantification

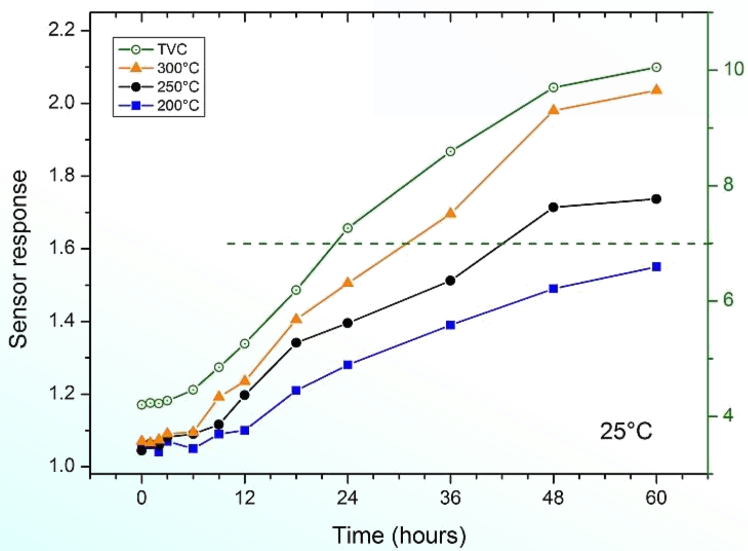


Agrifood products

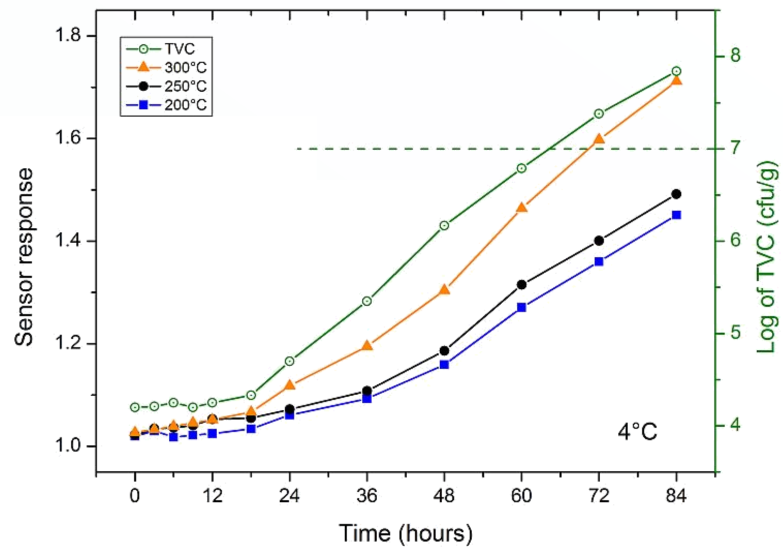


Rainbow trout

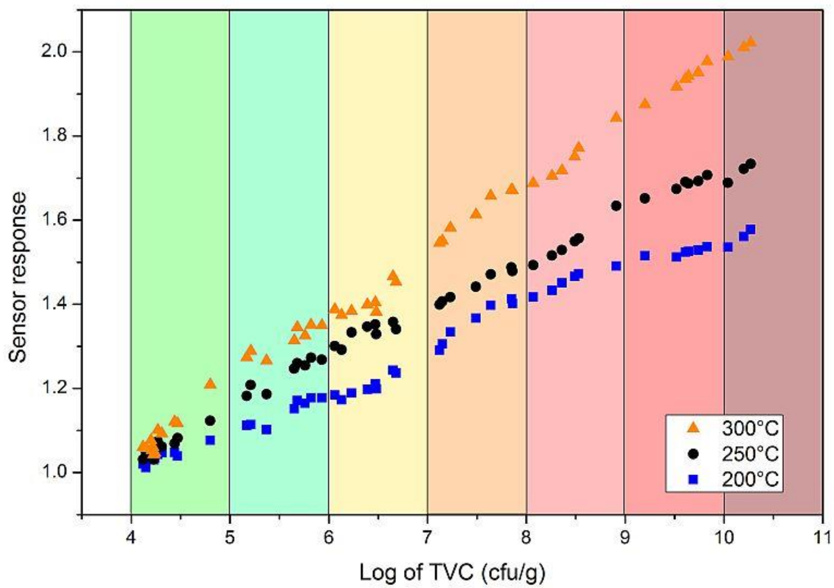
Room temperature

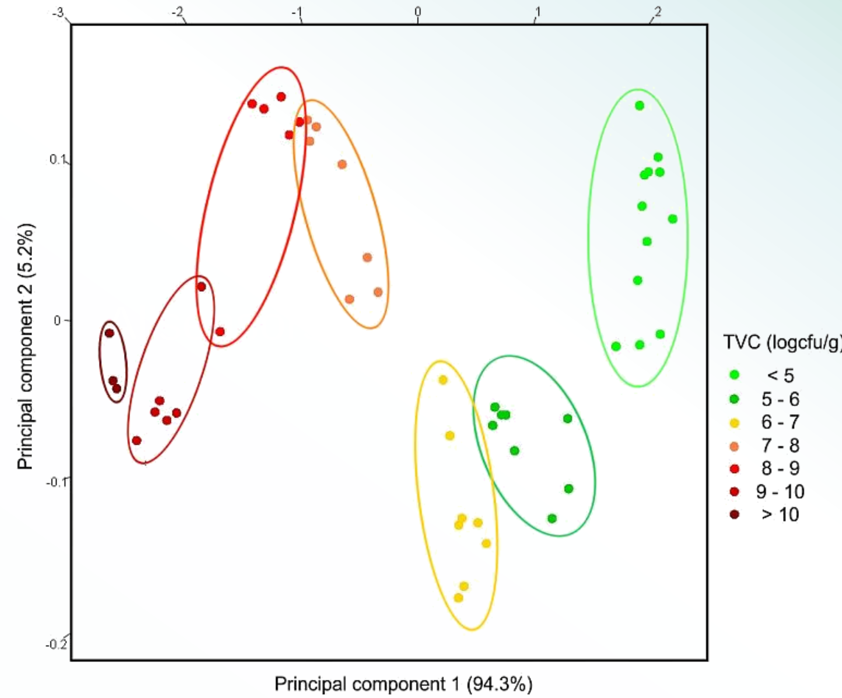


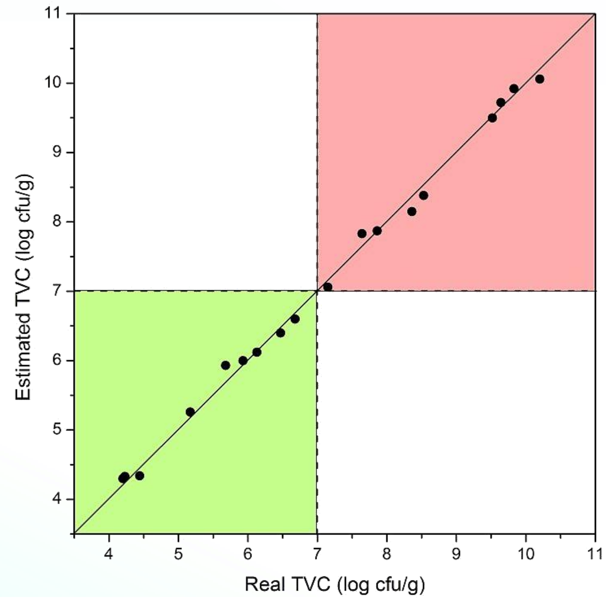
Refrigerator



Agrifood products







M. Tonezzer, N.X. Thai, F. Gasperi, N.V. Duy, F. Biasioli, Quantitative assessment of trout fish spoilage with a single nanowire gas sensor in a thermal gradient, Nanomaterials 2021, 11, 1604.

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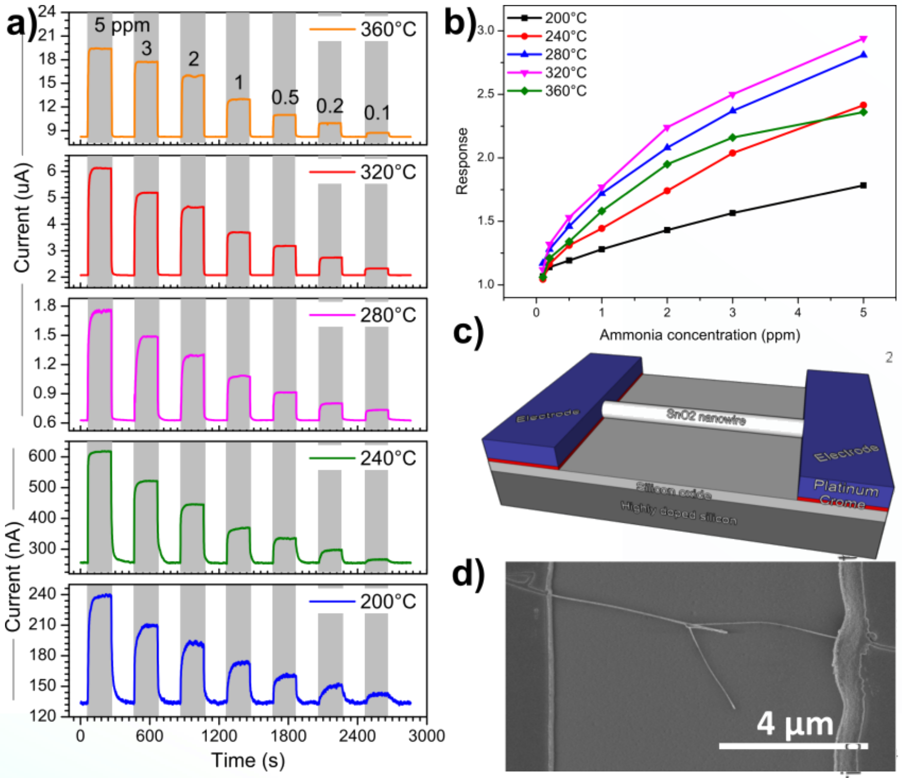
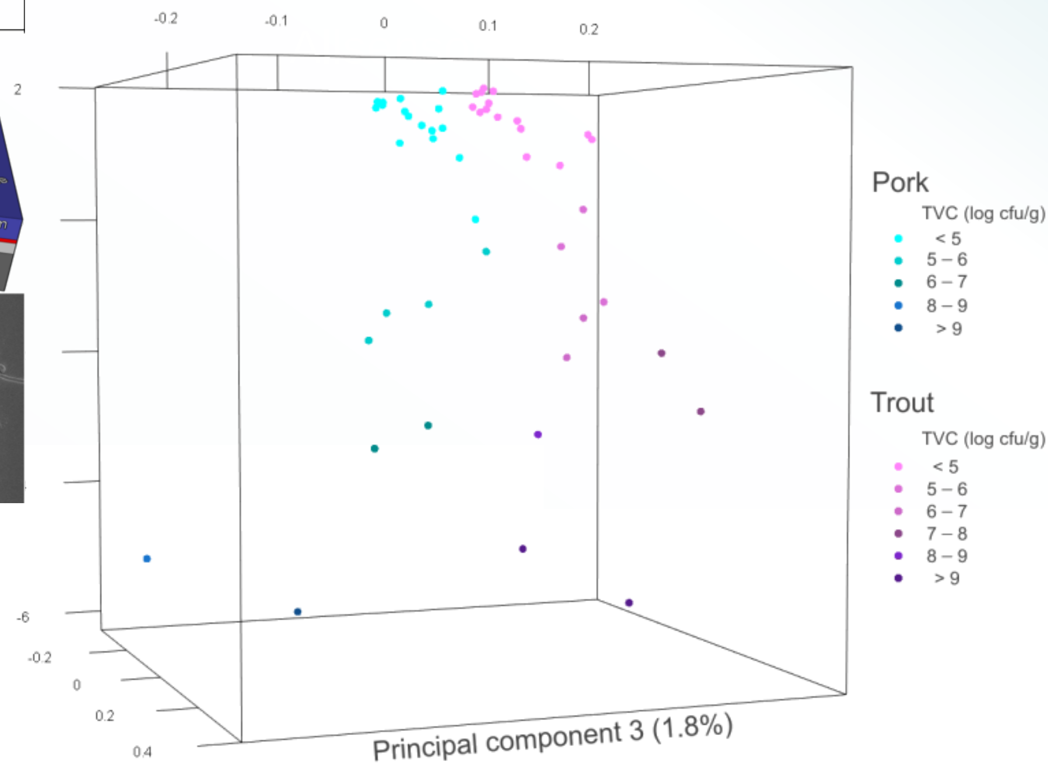
Agrifood products





M. Tonezzer,
Single nanowire gas sensor able to distinguish fish and meat and evaluate their degree of freshness,
Chemosensors 2021, 9, 249.

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Agrifood products

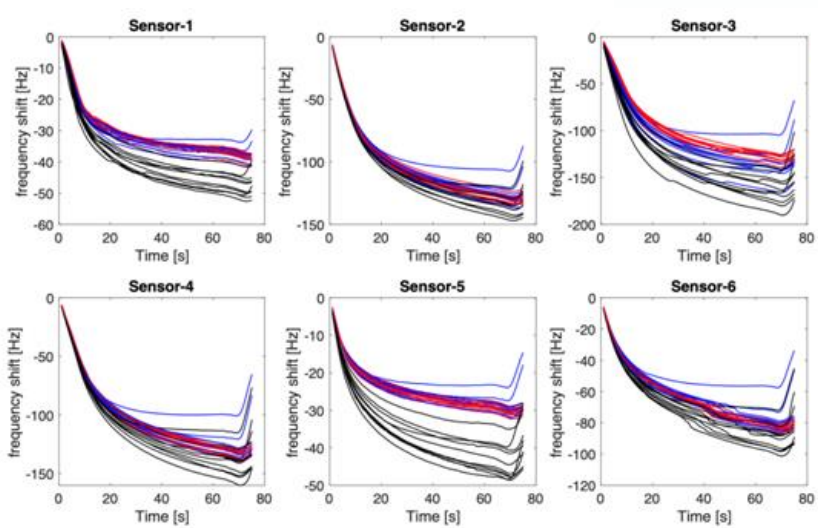
Trout	Estimated TVC (log cfu/g)						
		< 5	5 - 6	6 - 7	7 - 8	8 – 9	> 9
True TVC (log cfu/g)	< 5	9					
	5 – 6		3				
	6 – 7			2			
	7 – 8			1	2	1	
	8 – 9						1
	> 9						2

Pork	Estimated TVC (log cfu/g)						
		< 5	5 - 6	6 - 7	7 - 8	8 – 9	> 9
True TVC (log cfu/g)	< 5	9					
	5 – 6		4				
	6 – 7			2			
	7 – 8				2		
	8 – 9		1			2	
	> 9						1

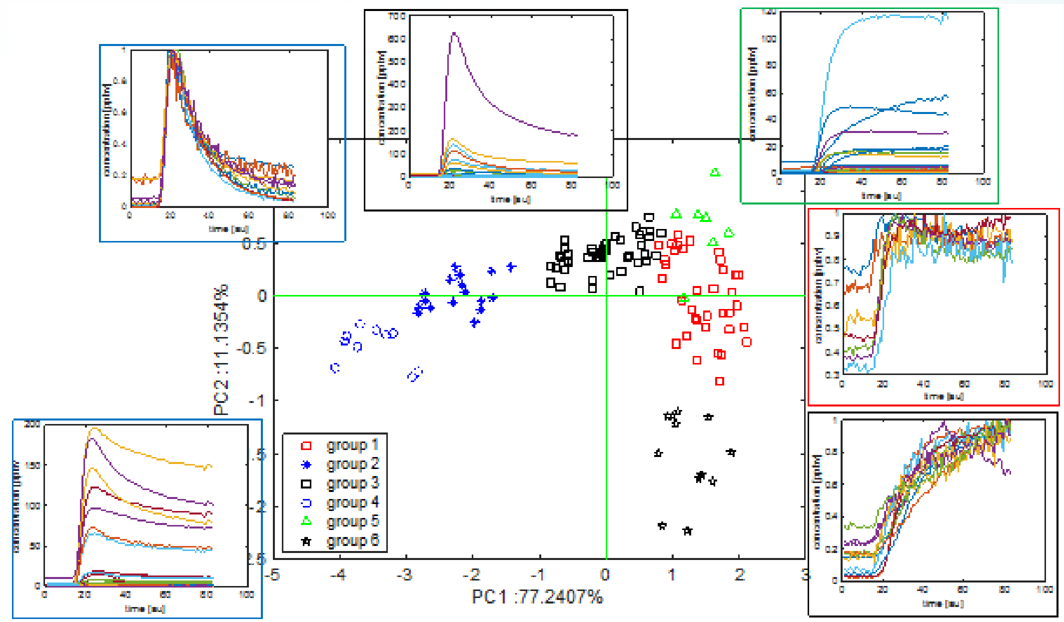
Sensors VS Proton Transfer Reaction – Mass Spectrometry

fresh
inoculated
+thyme oil

(Penicillium espansum)



sensor signal: always increasing



PTR-MS signal: different trends

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University of Tor Vergata

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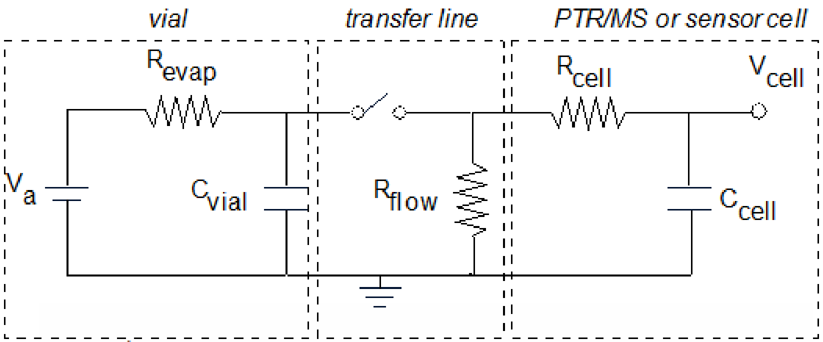
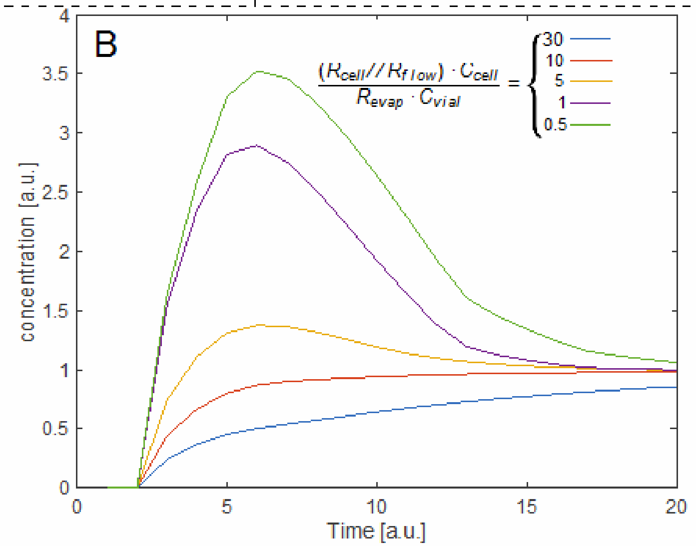
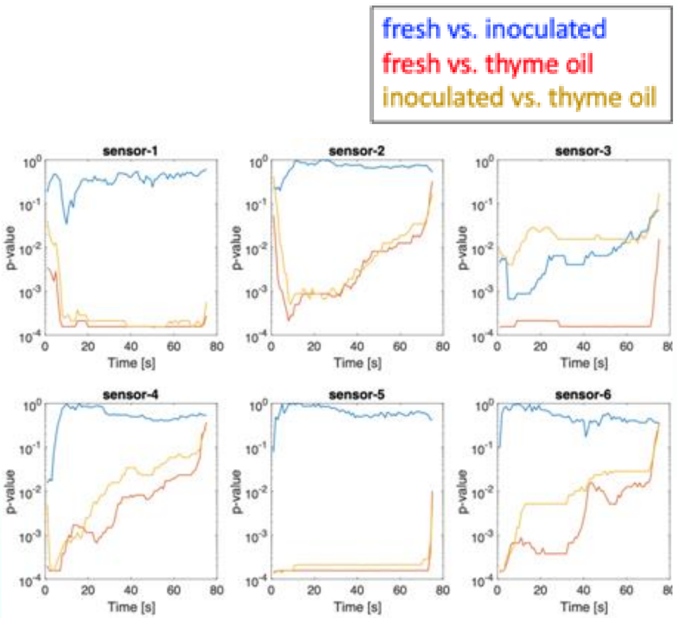
Equivalent electric circuit

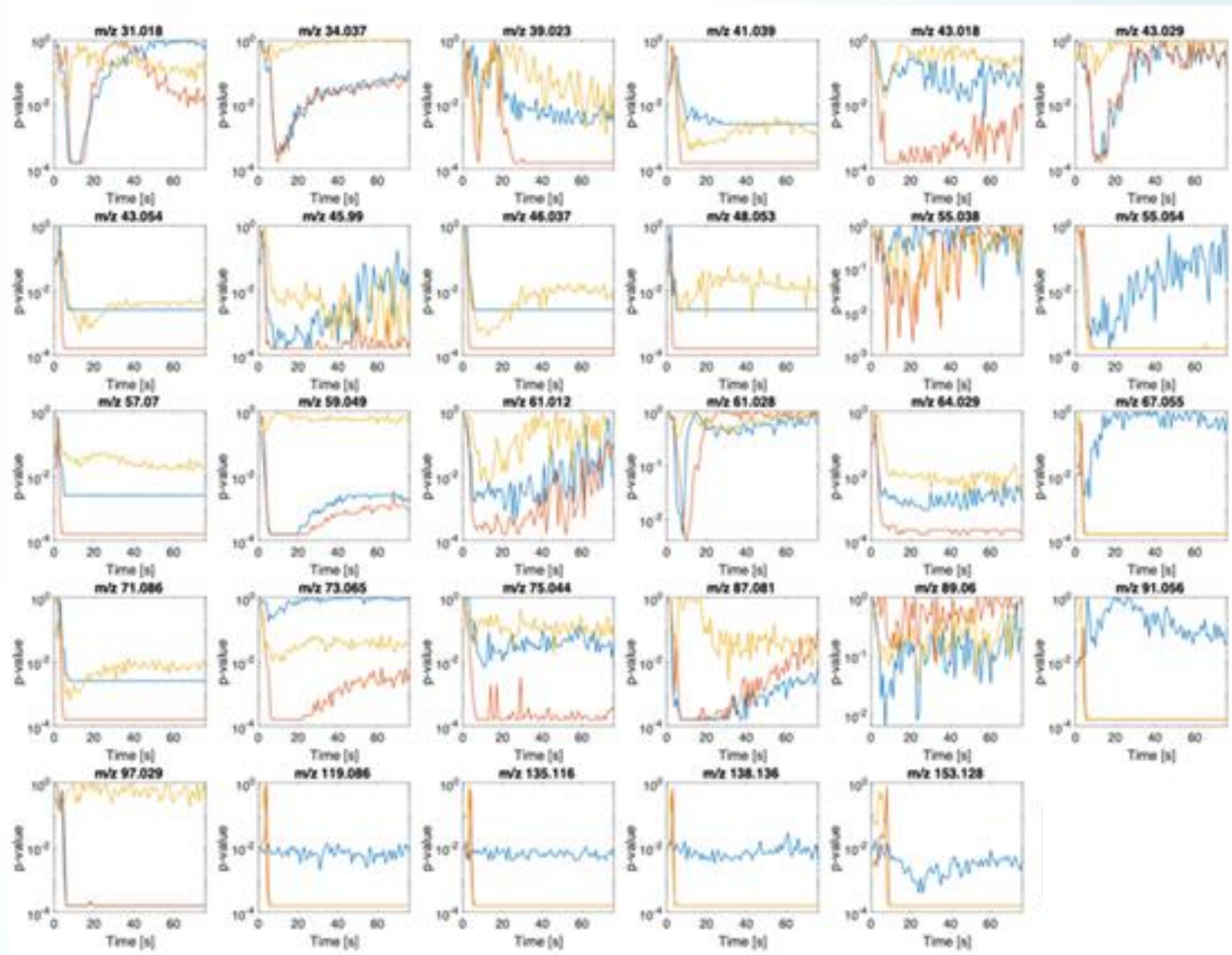




Electric quantity	Mass Transfer Quantity
Q (C)	Number of molecules (# of molecules)
I (A)	Flow of molecules (# of molecules/s)
V_A (V)	Saturation concentration (# of molecules/cm^3)
R_{EVAP} (Ω)	Inverse of evaporation volume transfer rate (s/cm^3)
C_{VIAL} (F)	Vial headspace volume (cm^3)
R_{FLOW} (Ω)	Inverse of carrier volume transfer rate (s/cm^3)
R_{CELL} (Ω)	Inverse of sensors cell filling volume transfer rate (s/cm^3)
C_{CELL} (F)	Sensors cell volume (cm^3)
V_{CELL} (V) = Q / C_{CELL}	Concentration in sensors cell (# of molecules/cm^3)

Discrimination performance

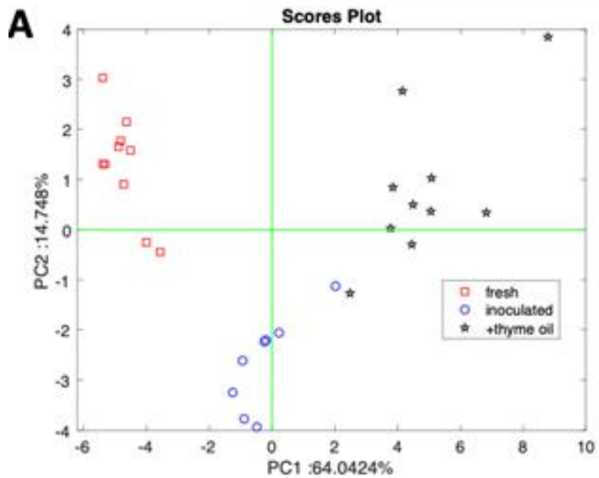


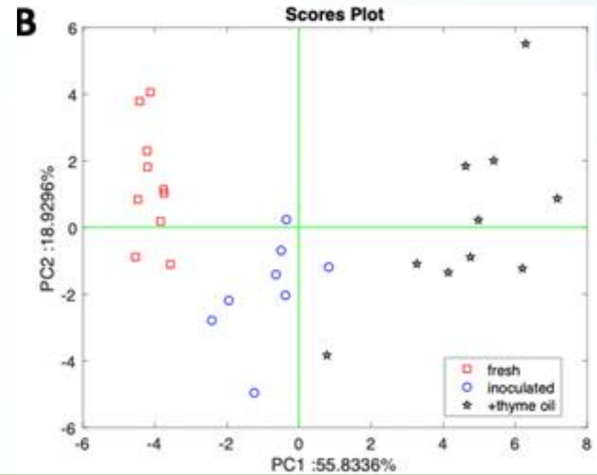


Discrimination performance

PTR-MS

10 s

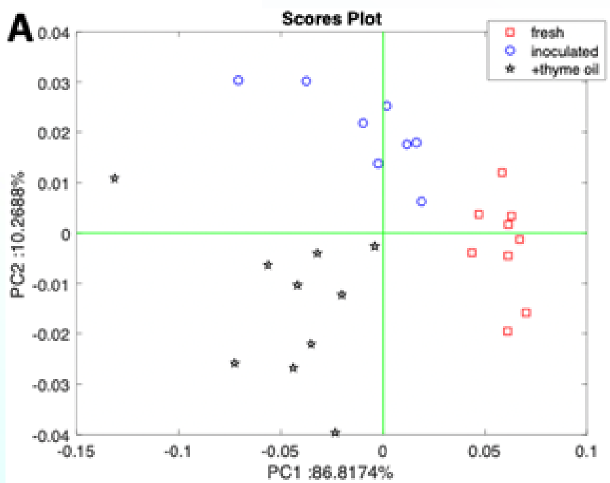


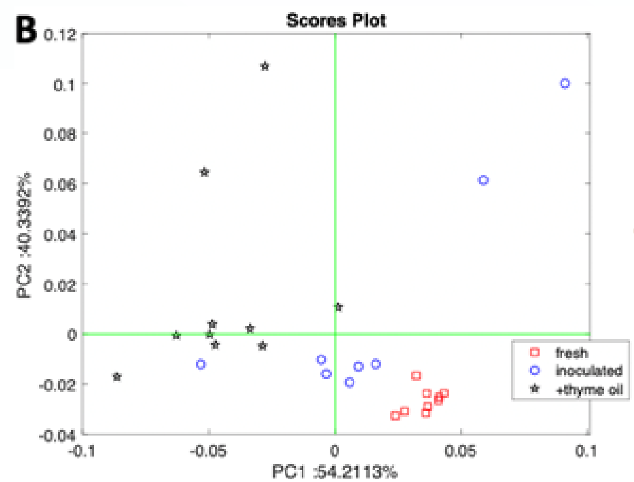


60s

sensors

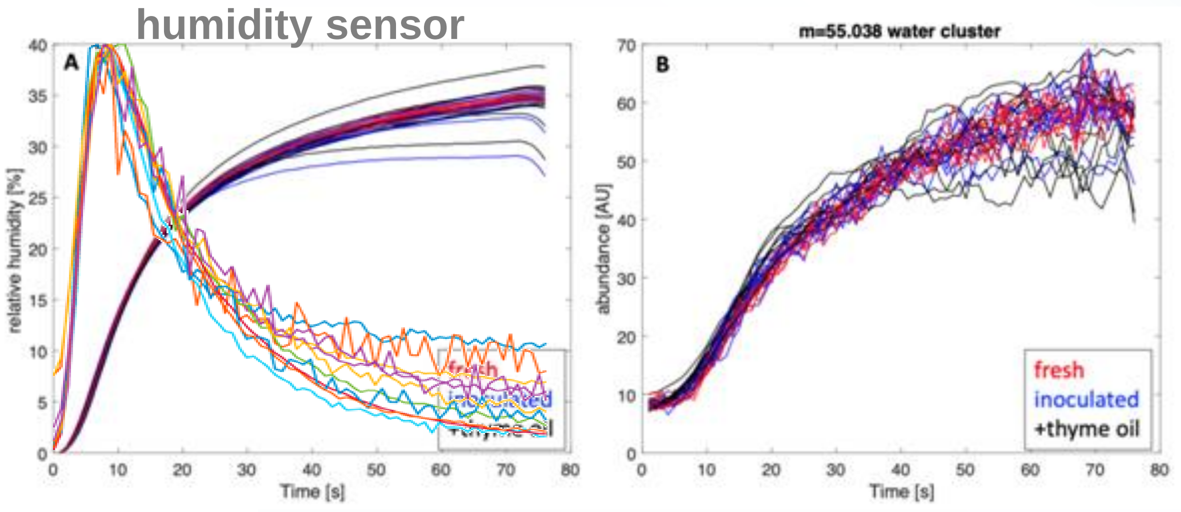
10 s





60s

Why?



the culprit is… <u>water vapor</u>

providing noise, not information

L. Quercia, I. Khomenko, R. Capuano et al.,
Optimization of gas sensors measurements by dynamic headspace analysis supported by simultaneous direct injection mass spectrometry,
Sensors and Actuators B: Chemical 347 (2021) 130580.

Conclusions

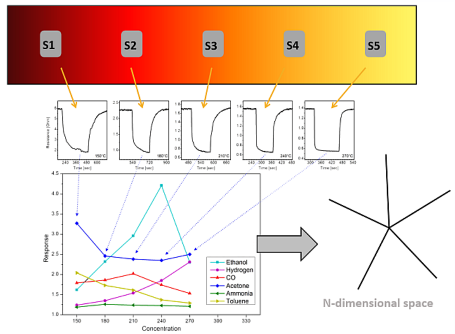
Thin Film Materials and Nanostructure Devices for Sensing Applications

Guest Editors
Dr. Hugo Aguas
Dr. Matteo Tonezzer

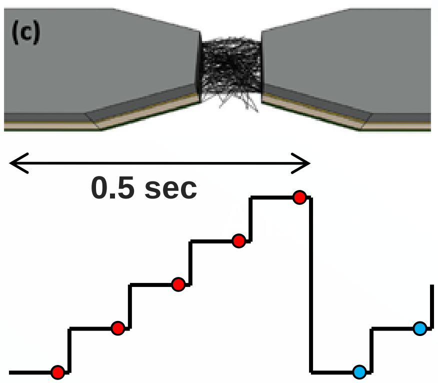
Deadline
31 January 2023

Special Issue
Invitation to submit

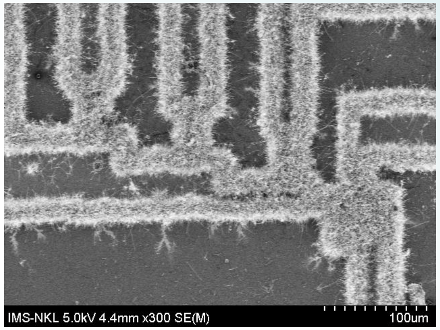
thermal gradient

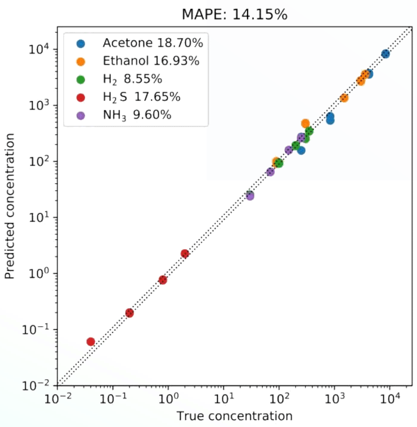


temporal gradient

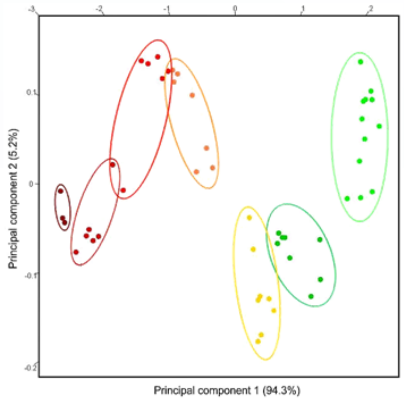


spatial gradient

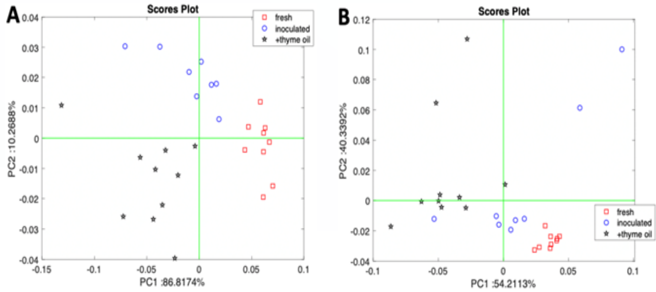




perfect classification
+
good estimation



food quality



PTR: right timing

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