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

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Collaboration

Institute of Materials for Electronics and Magnetism (IMEM)
Italian National Research Council (CNR)
Outline

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

The Food Production Chain

Panelists

Doctors

Preventive screening

Scientific instrumentation

Panelists

Doctors

Preventive screening
Tiny & smart gas sensors

Resistive sensors

Tiny
Cheap
Portable
Integrable

Gas chromatography
Mass-spectrometry

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.,
**Selectivity?**

“selectivity”

**Highly sensitive and selective** trimethylamine sensor using one-dimensional ZnO–Cr$_2$O$_3$ hetero-nanostructures, Nanotechnology 23 (2012) 245501.

![Gas response (Rd/Rg)](image)


![Gas response (Rd/Rg)](image)

**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.

Intrinsic vs Electronic Nose

~1000 odoral receptors (3% of genome)
Thermal gradient

S1, S2, S3, S4, S5

N-dimensional space
Thermal fingerprints

intrinsic selectivity

Prof. Nguyen Van Hieu
ITIMS – Hanoi University of Science and Technology
Multivariate statistics

Comp. 3
Comp. 2
Comp. 1

Hydrogen
Ethanol
CO
NH3
CO2
H2S
LPG

NO HCA
### Double-blind classification

#### Classification Methods
- **Support Vector Machine**
- **Random Forest Classification**
- **Logistic Regression**
- Classification Tree

#### Chemicals
- **CO**
- **CO₂**
- **Ethanol**
- **H₂**
- **H₂S**
- **LPG**
- **NH₃**

#### Cross-Class Matrix

<table>
<thead>
<tr>
<th></th>
<th>CO</th>
<th>CO₂</th>
<th>Ethanol</th>
<th>H₂</th>
<th>H₂S</th>
<th>LPG</th>
<th>NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>8</td>
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<td>CO₂</td>
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<td>H₂S</td>
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<tr>
<td>LPG</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Double-blind classification

classification tree

CO
13.9%, 5/36
T300

Air
29.4%, 5/17
T200

CO
26.3%, 5/19
T350

CO2
50.0%, 4/8
T200

CO2
50.0%, 4/8
T200

Air
55.6%, 5/9
T200

Air
55.6%, 5/9
T200

H2S
100%, 4/4

CO2
100%, 4/4

Air
100%, 5/5

LPG
100%, 4/4

NH3
100%, 4/4

CO
100%, 5/5

H2
100%, 5/5

Ethanol
50.0%, 5/10

Ethanol
50.0%, 5/10

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

200$^\circ$C

250$^\circ$C

300$^\circ$C

350$^\circ$C

400$^\circ$C

Benzene
Acetone
Hydrogen
Toluene
Ethanol

3.7%
19.3%
7.3%
35.3%
4.7%
Temporal gradient

“sandwich-oriented” growth

8mW  16mW  20mW

Temporal gradient

0.5 sec

H\textsubscript{2}S

Average error: 13.49%

NH\textsubscript{3}

Average error: 14.68%

H\textsubscript{2}

Average error: 16.80%

Ethanol

Average error: 16.35%

Acetone

Average error: 14.76%
Spatial gradient

classification

quantification

MAPE: 14.15%
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.
M. Tonezzer,
Single nanowire gas sensor able to distinguish fish and meat and evaluate their degree of freshness,
Chemosensors 2021, 9, 249.
# Agrifood products

## Pork

<table>
<thead>
<tr>
<th>True TVC (log cfu/g)</th>
<th>Estimated TVC (log cfu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 9</td>
<td></td>
</tr>
<tr>
<td>8 – 9</td>
<td>1</td>
</tr>
<tr>
<td>7 – 8</td>
<td>2</td>
</tr>
<tr>
<td>6 – 7</td>
<td>2</td>
</tr>
<tr>
<td>5 – 6</td>
<td>4</td>
</tr>
<tr>
<td>&lt; 5</td>
<td>9</td>
</tr>
</tbody>
</table>

## Trout

<table>
<thead>
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<td>2</td>
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<tr>
<td>5 – 6</td>
<td>3</td>
</tr>
<tr>
<td>&lt; 5</td>
<td>9</td>
</tr>
</tbody>
</table>
Sensors VS Proton Transfer Reaction – Mass Spectrometry

(sensor signal: always increasing)

(Penicillium espansum)

(PTR-MS signal: different trends)

Prof. Corrado Di Natale
University of Tor Vergata
Equivalent electric circuit

<table>
<thead>
<tr>
<th>Electric quantity</th>
<th>Mass Transfer Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q (C)</td>
<td>Number of molecules (# of molecules)</td>
</tr>
<tr>
<td>I (A)</td>
<td>Flow of molecules (# of molecules/s)</td>
</tr>
<tr>
<td>V_A (V)</td>
<td>Saturation concentration (# of molecules/cm^3)</td>
</tr>
<tr>
<td>R_EVAP (Ω)</td>
<td>Inverse of evaporation volume transfer rate (s/cm^3)</td>
</tr>
<tr>
<td>C_VIAL (F)</td>
<td>Vial headspace volume (cm^3)</td>
</tr>
<tr>
<td>R_FLOW (Ω)</td>
<td>Inverse of carrier volume transfer rate (s/cm^3)</td>
</tr>
<tr>
<td>R_CELL (Ω)</td>
<td>Inverse of sensors cell filling volume transfer rate (s/cm^3)</td>
</tr>
<tr>
<td>C_CELL (F)</td>
<td>Sensors cell volume (cm^3)</td>
</tr>
<tr>
<td>V_CELL (V) = Q / C_CELL</td>
<td>Concentration in sensors cell (# of molecules/cm^3)</td>
</tr>
</tbody>
</table>
Discrimination performance
Discrimination performance

**PTR-MS**

10 s

60 s

**Sensors**

10 s

60 s
Why?

the culprit is… water vapor

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

- **thermal gradient**
- **temporal gradient**
- **spatial gradient**

Perfect classification + good estimation

Food quality

PTR: right timing

mape: 14.15%

Guest Editors
Dr. Hugo Aguas
Dr. Matteo Tonezzer

Deadline
31 January 2023

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