PZT MicroCantilever Sensors for VOCs

Enose in Agriculture

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Contents

- Application: detecting rot in potato storage
- Piezo-microcantilevers as electronic nose
- Readout Strategies: Noise in Practice

Project Participants

Partners

UNIVERSITY OF TWENTE.
Potato Storage

- Matching supply & demand requires storage on site
- Storage time ~1 year
- New harvest is still wet and vulnerable to rot
- Rot spreads very quickly
- First few weeks are critical
  - Monitoring is needed
Potato Storage Systems

- Warehouses are ventilated with active cooling
- Control of Temperature (and partially Humidity)
- $\text{CO}_2$ is also monitored

30% losses without warehousing system

Big problem in e.g. developing world...
Potato Storage Systems

Multiple T and RH Sensors

Automatic Recipes

Energy Minimization

Can Track Batch from Field to Customer
Add one more sensor

- Monitors gas composition in real time
- Early warning for disease

Challenges (specs):
- Ppm detection limit
- T and RH compensated
- Position, sampling?
Noninvasive detection of lung cancer by analysis of exhaled breath

Batajevic et al.
BMC Cancer 2009 9:348
Types of Gas Detection Principles

Analytical: direct molecule detection

Chromatography
Spectrometry

Semi-Analytical: Inverse Mixing Models (only for known few-component compositions)

Response to Ethanol

Response to Humidity

TWO SENSORS $S_1 \neq S_2$
Types of Gas Detection Principles

Chemometrics (Enose)
E-Nose Working Principle

Human olfactory system

e-nose: array of non-specific, cross-reactive sensors combined with an information processing system

Many Sensors of “Some” Specificity

Complex Analyte

Statistical Analysis
E-Nose Detector System

Sensor Array → Feature Extraction and Preprocessing → Dimensionality Reduction → Classification/Prediction/Clustering → Decision Making

Feedback/Adaptation

Post-processed Odor class

Raw Measurements → Normalized Vector → Feature Vector → Odor Class (confidence level)
Typical Signals from an Enose Sensor: Beer varieties

Features:
1. Height of response
2. Time constants
   - Multi-exp fits

Challenges @ low conc.
- Sensitivity of fits to drifts
- Selectivity: can we distinguish an analyte in a large gas background

Odour signature for hops variety Amarillo
Commercially Available Enose Instruments

**Owlstone Lonestar**
(Field Assymmetric Ion Mobility) FAIMS

**Karlsruhe Institute of Tech.**
(room-T oxide nanowire array)

**Airsense**
(heated mox sensor array)

**Various Benchtop Chromatography Devices**

**Inside the Cyanose® 320**

Sample in jet
Pneumatic Pump

Digital Ports (RS 232 and USB)

Sensor Array

**Cyanose**
(array of NP-doped polymers)

**ETC.**
Detection of Potato Storage Disease via Gas Analysis: A Pilot Study Using Field Asymmetric Ion Mobility Spectrometry

Massimo Rutolo \(^1\), James A. Covington \(^1\), John Clarkson \(^2\) and Daciana Iliescu \(^1\)

*Sensors 2014, 14, 15939-15952; doi:10.3390/s140915939*
Olfactory Detection of Rot

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Gas ions mobility spectra

Many Literature Studies dating back to 1990s

Different Types of Rot

Different Biomarkers

VOC Fingerprinting

This line is selected for highest observability.

Statistical analysis (PCA) and Clustering
Olfactory Detection of Rot

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Many Literature Studies dating back to 1990s

Different Types of Rot

Different Biomarkers

VOC Fingerprinting
Olfactory Detection of Rot

The development of a sensor system for the early detection of soft rot in stored potato tubers

To cite this article: B P J de Lacy Costello et al 2000 Meas. Sci. Technol. 11 1685

Many Literature Studies dating back to 1990s

Different Types of Rot

Different Biomarkers

VOC Fingerprinting

VOC onderzoek aardappelen - Conceptrapport

VOC Biomarkers

2015-2016 Bastiaan Brouwer, Matthijs Monisma

Different positions in a crate
Potato Storage Systems

Analytical/Instrument Based

- Distribute sampling tubing inside the stored potatoes
- (similar to T probes)
- Gas samples brought to a central instrument
Potato Storage Systems

Chip-based Dispersed Disposables

- Distribute sensing chips inside the storage
- Sensors communicate measured data periodically
- Can be salvaged later
MicroCantilever Principle

Sorption changes
Mass & Spring constant
⇒ Resonant f shift
\[ \frac{f}{f} = \frac{1}{2} \left( \frac{k}{k} - \frac{m}{m} \right) \]
Piezoelectric MEMS cantilever with PZT Layer

- Silicon
- SiO$_2$
- Pt
- Photoresist
- PZT
- Insulation
- Gold
- Pyralin

200um
SURFACE MASS LIMIT OF DETECTION SMLOD
* Thermomechanical Noise Limit *
In practice, limit is due to electronic noise

\[
\frac{\Delta m}{S}_{\text{min}} \approx h \rho v \sqrt{\frac{Bk_B T}{\pi^2 A^2 m_b Q f_n^3}}
\]

A=Displacement amplitude

<table>
<thead>
<tr>
<th>Device &amp; Ref</th>
<th>Device area</th>
<th>Resonance Frequency</th>
<th>Quality factor</th>
<th>Surface sensitivity</th>
<th>Minimum Relative Frequency deviation</th>
<th>SMLOD</th>
<th>DMMP Concentration resolution (measured)</th>
<th>DMMP Concentration resolution (estimated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FBAR [122]</td>
<td>$5 \times 10^4 , \text{(b)}$</td>
<td>1100 (a)</td>
<td>210 (a)</td>
<td>726 (a)</td>
<td>$3.6 \times 10^{-7} , \text{(b)}$</td>
<td>10000 (b)</td>
<td>(c)</td>
<td>60 (e)</td>
</tr>
<tr>
<td>SAW [34]</td>
<td>$5 \times 10^7 , \text{(b)}$</td>
<td>158 (a)</td>
<td>(c)</td>
<td>100 (a)</td>
<td>$7 \times 10^{-8} , \text{(a)}$</td>
<td>7000 (b)</td>
<td>(b)</td>
<td>42 (a)</td>
</tr>
<tr>
<td>CMR [123]</td>
<td>$6 \times 10^3 , \text{(b)}$</td>
<td>180 (a)</td>
<td>$5 \times 10^4 , \text{(a)}$</td>
<td>$2.3 \times 10^3 , \text{(b)}$</td>
<td>$1.3 \times 10^{-8} , \text{(a)}$</td>
<td>60 (a)</td>
<td>700 (d)</td>
<td>0.35 (e)</td>
</tr>
<tr>
<td>CMUT [124]</td>
<td>$1 \times 10^6 , \text{(b)}$</td>
<td>47.7 (a)</td>
<td>140 (a)</td>
<td>$4.1 \times 10^3 , \text{(b)}$</td>
<td>$1.15 \times 10^{-8} , \text{(a)}$</td>
<td>80.5 (a)</td>
<td>(d)</td>
<td>3 (e)</td>
</tr>
<tr>
<td>Nanocantilevers [50]</td>
<td>1.5 (a)</td>
<td>10 (a)</td>
<td>200 (a)</td>
<td>$3.75 \times 10^3 , \text{(b)}$</td>
<td>$1.5 \times 10^7 , \text{(a)}$</td>
<td>400 (b)</td>
<td>(c)</td>
<td>80 (e)</td>
</tr>
<tr>
<td>$\mu$-cantilevers [125][126]</td>
<td>$3.2 \times 10^3 , \text{(b)}$</td>
<td>0.1 (a)</td>
<td>80 (a)</td>
<td>$2.8 \times 10^3 , \text{(b)}$</td>
<td>$10^{-8} , \text{(a)}$</td>
<td>53 (a)</td>
<td>25 (d)</td>
<td>2 (e)</td>
</tr>
</tbody>
</table>


PZT offers high transduction factors
⇒ Higher electronic amplitudes
⇒ Less electronic noise in practice
Electronic Readout

Mechanical resonance Transduced by PZT

parasitic

Series peak resonance influenced by “motional” parts
Electronic Readout

Mechanical resonance Transduced by PZT

parasitic

parasitic

\[ \text{capacitance ratio } \alpha = \frac{C_p}{C} = 10^{-2} \]
Readout and Measurements: Phase-Locked Loop (PLL)

- **Control**
- **Analyze**

Phase-Lock-Loop Resonator Interface

- Tracks resonant $f$ automatically
- mHz noise with these sensors
- Complex to implement in product
- Suffers from $C_P$ variation

- Mechanical resonance
- Transduced by PZT
- Parasitic $C_P$
**Impedance Peak** Resonator Interface

+ Simple to implement
+ Sequential readout with a switch matrix easier to implement
- Unknown noise/speed curve
- Also suffers from $C_p$ variation

\[
\begin{align*}
  f_{\text{series}} &= \frac{1}{2} \sqrt{\frac{k}{LC}} \sqrt{\frac{k}{m}} \\
  f_{\text{parallel}} &= \frac{1}{2} \sqrt{\frac{1}{L(C || C_p)}}
\end{align*}
\]
Readout and Measurements

Measured Frequency Noise of a Piezo-Cantilever using the PLL Method
(resonance $f = 141558$ Hz, 60s data record @ 200 S/s for each point in the graph)

- Frequency Noise [Hz]
- Measurement Bandwidth [Hz]
- Measured Frequency Noise:
  - White noise:
    - $\Delta f/f = 5 \cdot 10^{-6}$
    - @ 1min interval!
  - Power-law noise:

\[
\frac{\Delta m}{m_{eff}} = 2 \frac{\Delta f}{f} \Rightarrow \left( \frac{\Delta m}{S} \right)_{\text{min}} \approx 100 \frac{\text{ag}}{\mu\text{m}^2}
\]

Practical SMLOD (on a 1min data record)
Measurements: ACETONE in N₂

\[ S_{PEI} = 4 \frac{\text{mHz}}{\text{ppm}} \quad S_{PAA} = 2 \frac{\text{mHz}}{\text{ppm}} \]

Noise of 80mHz then corresponds to a Limit of Detection of 20ppm over 1 min.
Noise Types

“DOES NOT EXIST”
- Decreases with $\sqrt{t_m}$
- Curve-Fit Algos don’t see it

LIMITS IN PRACTICE

INDEPENDENT ON MEASUREMENT TIME

INCREASES WITH MEASUREMENT TIME
## Resonant Sensor Noise Sources

<table>
<thead>
<tr>
<th>THERMO-MECHANICAL NOISE</th>
<th>ELECTRONIC NOISE</th>
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<tbody>
<tr>
<td>- White Power Spectrum</td>
<td>- White Power Spectrum</td>
</tr>
<tr>
<td>- Due to Intrinsic Acoustic Losses</td>
<td>- + 1/f + 1/f^2 + ... Power Spectrum</td>
</tr>
<tr>
<td>- Due to Air Friction</td>
<td>- Due to Intrinsic Electronic Losses</td>
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<th>THERMAL FLUCTIATION NOISE</th>
<th>DIFFUSION AND ABSORPTION/DESORPTION NOISE</th>
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<td>- White Power Spectrum</td>
<td>- Complex Power Spectrum</td>
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<tr>
<td>- Due to Sensitivity of ω₀ on T</td>
<td>- Due to Ab/De-sorption &amp; Diffusion of Species Along the Surface</td>
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</table>
Resonant Sensor Noise Sources

**THERMO-MECHANICAL NOISE**
- White Power Spectrum
- Due to Intrinsic Acoustic Losses
- Due to Air Friction

**THERMAL FLUCTIATION NOISE**
- White Power Spectrum
- Due to Sensitivity of $\omega_0$ on $T$

**ELECTRONIC NOISE**
- White Power Spectrum
- + $1/f + 1/f^2 + ...$ Power Spectrum
- Due to Intrinsic Electronic Losses

**DIFFUSION AND ABSORPTION/DESORPTION NOISE**
- Complex Power Spectrum
- Due to Ab/De-sorption & Diffusion of Species Along the Surface

LIMITS IN PRACTICE!
If we want to detect concentration levels: 20ppm but a calibrant is needed (few min total measurement time allowed)

Minimum uncertainty 79mHz
Resonator Noise Analysis: Allan Deviation

EXPECTED INNACURACY BETWEEN NEIGHBOURING MEASUREMENTS

If we want to detect concentration rate changes: 1.5ppm/sec
Resonator Noise Analysis: Allan Deviation

EXPECTED INNACURACY BETWEEN NEIGHBOURING MEASUREMENTS

If we want to detect concentration rate changes: 3ppm/10 sec, etc..
Resonator Noise Analysis: Allan Deviation

Detecting Rot in Potatoes:

Via Concentration Levels
• 1ppm
• Can’t detect (limit is 20ppm)

Via Concentration Rate Change
• 1ppm/4days = 2.9 ppb/1000s
• Extrapolating the graph $10^{11}$ s (3 kyears) of measurement time needed
• Can’t detect
Conclusions and Recommendations

Detection of potato rot via E-nose is present in literature and prior work.

Our micro-cantilevers with PZT have:
- An SMLOD comparable to literature
- But a lot of “colored” noise making the LOD in the single-double digit ppm (1ppm is needed)

Strategies to reach required LOD:
- Increase chemical sensitivity (absorption per unit surface) to analyte gas by more than 10 times
- Increase mass sensitivity df/dm via light & stiff cantilevers by 10 times
- Reduce both 1/f (pink) and 1/f² (brown) noise by more than 10 times
- Improving Q-factor is not a priority; find ways to increase max. amplitude instead
Many Thanks to:

Ruud Steenwelle
Albert van Hoorn

and all students that contributed greatly.

Questions?