New Approaches to Chemical Sensing:
Artificial Olfactory Mucosa & Info-chemical Communication

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“An electronic nose is an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognising simple or complex odours.”

Chemical sensors suffer from noise

Noise comes from natural variation in parameters and averages over time to zero

Examples:

- Johnson noise, Shot noise, flicker noise
- Sample errors
- Digital bit error
- Chemical noise is often 1/f noise
- Parameter S/N

Chemical sensors suffer from interference

Interference comes from parameters dependent on other variables (can be modelled)

Examples:

• Ambient temperature
• Ambient humidity
• Atmospheric oxygen
• Parameter $\Delta S = (dS/dC)\Delta C + (dS/dI)\Delta I (<10^4$ for humidity)

Source: Searle et al. 2002 IEEE Sensors Journal 2 218
Chemical sensors suffer from drift

Variation over time of signals and parameters

Examples:

- Aging of sample
- Baseline or response of sensor
- Parametric drift
- Aging of sensor material
- Poisoning of sensor
- Parameter: $\frac{dS}{dt}$

Source: Searle et al. 2002 IEEE Sensors Journal 2 218
Pre-processing algorithms help ...

Feature selection:

- For additive interferences use differential signal \((S_2 - S_1)\)
- For multiplicative interferences use signal ratio \(S_2/S_1\)
Time-dependent sensor models help ..

Use **transient** properties of sensor signal to extract more information – not possible with mass spectrometers and DNA chips.

- Include time-constants in the sensor model for dynamical model
- Create linear and non-linear models

Source: Hines et al 1999 *Proc. IEE: Circuits, Systems and Devices* **146** 297-310
Any challenges left in chemical sensing?

Umm the Euro …
## Depends on Problem ….

<table>
<thead>
<tr>
<th>Measurand</th>
<th>Reference odour?</th>
<th>Odour stability?</th>
<th>Vapour pressure</th>
<th>Number of components</th>
<th>Level of difficulty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple odours, e.g. ethanol</td>
<td>Yes</td>
<td>Good</td>
<td>High</td>
<td>One</td>
<td>Low</td>
</tr>
<tr>
<td>Solvents in polymers, paints, plastics etc.</td>
<td>Yes</td>
<td>Good</td>
<td>High</td>
<td>Several</td>
<td>Low</td>
</tr>
<tr>
<td>Perfumes/essential oils</td>
<td>Some</td>
<td>OK</td>
<td>High</td>
<td>Several</td>
<td>Medium</td>
</tr>
<tr>
<td>Food: Coffee quality</td>
<td>No</td>
<td>Poor</td>
<td>Medium</td>
<td>100’s</td>
<td>Medium</td>
</tr>
<tr>
<td>Explosive materials (plastic)</td>
<td>Yes</td>
<td>Good</td>
<td>Very Low</td>
<td>Several</td>
<td>High</td>
</tr>
<tr>
<td>Human odours</td>
<td>No</td>
<td>Poor</td>
<td>Low</td>
<td>100’s</td>
<td>High</td>
</tr>
</tbody>
</table>

Remote environmental gas sensing

• Need **low-cost** detection of **low** levels of chemicals (<10 ppm) in atmospheric air

• Need **rapid** response of sensors for normal use (1’s not 10’s to 100’s)

• Perhaps need to **locate** source of gas so mobile (ms)
Detection of underground mines

- 100 millions of mines in world
- Different types of mines
- Variable terrain
- Poor countries
- Extremely low vapour pressures of plastic explosives
Detection of hidden explosives needed

- Explosives in airport luggage
- Fast and reliable detection needed
- Trace levels with variable background
- Different materials (nitrates and peroxides)
Trace level explosive materials

EUNetAir – Low cost please?

Detection limit in g/ml

10^-15
10^-14
10^-13
10^-12
10^-11
10^-10
10^-9
10^-8
10^-7
10^-6

Basic e-nose

E-nose with SPME

Mass Spec.

HPLC

MS-Cl

Airport sniffer

Electron capture

Ion mobility spectrometer

Fluorescent polymer

Humidity mg/ml
New Approaches: Gas/Odour Microsensors

Nanomaterials
• Metal oxides
• CNTs
• Polymers

CMOS gas sensors
• Resistive
• Calorimetric
• Thermal modulation

Artificial e-mucosa and Ratiometric chemoreception

Source: Santra et al 2010 Sensors and Actuators B 146 559
Source: Santra et al 2010 Nanotechnology 21 1
Iwaki et al 2009 IEEE Sensors Journal 9 314
Human Olfactory Mucosa

Distributed array of olfactory cells along mucous coated nasal cavity
Warwick E-mucosa

Source: Sanchez-Montanes et al 2008 *Proc. Roy. Soc. A*, 464
Large CMOS sensor arrays

- 5 rows by 14 columns 70 resistive and 70 FET sensors
- Each row is deposited with a different polymer to increase discrimination capability

Polymer deposition:
- PVPH
- PCL
- PEVA
- PSB
- PEG
25 x 12 Sensor Array Response to Oils – Convolution between front and back arrays


No baseline signal used
INSECT-BASED INFO-CHEMICAL COMMUNICATION SYSTEM (iCHEM)
Insect-Based Chemoreception
Ratiometric detection of molecules

### Example: Fruit volatiles

<table>
<thead>
<tr>
<th>Chemical</th>
<th>GC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>butyl hexanoate</td>
<td>37</td>
</tr>
<tr>
<td>pentyl hexanoate</td>
<td>5</td>
</tr>
<tr>
<td>propyl hexanoate</td>
<td>4</td>
</tr>
<tr>
<td>butyl butanoate</td>
<td>10</td>
</tr>
<tr>
<td>hexyl butanoate</td>
<td>44</td>
</tr>
<tr>
<td>butyl hexanoate</td>
<td>0.01</td>
</tr>
<tr>
<td>3-methylbutan-1-ol</td>
<td>4</td>
</tr>
<tr>
<td>isoamyl acetate</td>
<td>1.5</td>
</tr>
<tr>
<td>4,8-dimethyl-1,3(E),7-nonatriene</td>
<td>0.09</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>94.3</td>
</tr>
<tr>
<td>dihydro-β-ionone</td>
<td>0.10</td>
</tr>
<tr>
<td>β-caryophyllene</td>
<td>5.8</td>
</tr>
<tr>
<td>3-methylbutan-1-ol</td>
<td>27.5</td>
</tr>
<tr>
<td>isoamyl acetate</td>
<td>0.9</td>
</tr>
<tr>
<td>1-octen-3-ol</td>
<td>9</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>54.9</td>
</tr>
<tr>
<td>dimethyl trisulfide</td>
<td>1.9</td>
</tr>
</tbody>
</table>

*(Linn et. al, 2005)*
Quartz Crystal Microbalance (QCM)

Operational Mechanism: Sauerbrey equation

\[ \Delta f = -\frac{2 f_0^2}{A \sqrt{\rho_q \mu_q}} m_f \]

Sensitivity: \( \Delta f = 7.2 \text{ Hz/ng} \)

AC

Gas sensitive coating

Gold electrode

Quartz crystal

Gold electrode

3 mm
Ligand detection using QCMs

Odorant | PSF | PSB | PEG | PMMA
---|---|---|---|---
3m | 137 | 144 | 110 | 42
HB | 127 | 103 | 58 | 29
EA | 136 | 57 | 35 | 28
BH | 134 | 87 | 33 | 32
BH | 59 | 77 | 26 | 15
HB | 98 | 127 | 31 | 14
EA | 157 | 28 | 59 | 26
3m | 90 | 39 | 46 | 18
3m | 80 | 39 | 49 | 16
HB | 82 | 138 | 57 | 24
BH | 69 | 118 | 53 | 22
EA | 130 | 33 | 31 | 22

DF1: 40.3%
DF2: 30.9%
Ratiometric Compounds: Quad Array of Dual 262 MHz SAWR

Filter Board
Oscillat or circuitry

JLMQ interfaces
Polymer coated QCM arrays
Odor chamber
µEvaporator
µEvaporator controller

SAW array

Pheromones in air: Poster P2.2.12 Thomas et al. IMCS 2012
Ratiometric decoding using sensor responses

Source: Sensors and Actuators at press
Neuromorphic FPGA of Insect Antennal Lobe

Source: Racz et al Int J Circuit Theory and Applications 2012 at press
Real-time Chemical Communication

http://www.youtube.com/watch?v=IBLN3sCbbPY

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Finally .. Cell-based Sensors

<table>
<thead>
<tr>
<th>Feature</th>
<th>Thickness [nm]</th>
<th>Frequency [MHz]</th>
<th>Feature size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-D-lysine</td>
<td>15</td>
<td>39,901</td>
<td>26</td>
</tr>
<tr>
<td>Bilipid layer</td>
<td>22.5</td>
<td>26,600</td>
<td>39</td>
</tr>
<tr>
<td>Edge of cell</td>
<td>615</td>
<td>973</td>
<td>1,069</td>
</tr>
<tr>
<td>Middle of cell</td>
<td>7,515</td>
<td>80</td>
<td>13,064</td>
</tr>
<tr>
<td>Upright cell</td>
<td>15,015</td>
<td>40</td>
<td>26,102</td>
</tr>
</tbody>
</table>

Source: Racz et al Int J Circuit Theory and Applications 2012 at press
Cell based SAW sensor for Ligands

SAW device

HEK cells on SAW device

Cell deposition

Liquid chamber

20 μm

2.5 μm

HEK cells on SAW device

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EU NetAir (Special Session), Nuremberg, May 2012
Conclusions – New Approaches Please

• Real-world low-cost environmental monitoring is challenging

• Current methods are often lab based, slow and expensive – hence EU NetAir project

• Biologically-inspired solutions may help?
  • Artificial olfactory mucosa with convolution based signal processing
    • **Differential and Drift Rejection**

• Info-chemical receivers based on classifying ratiometrically-encoded molecules
  • **Differential and Ratiometric, Fast, Low-cost and Noise Rejection**
REFERENCES


13. Poster P2.2.12: Thomas et al. IMCS 2012