New Approaches to Chemical Sensing:

Artificial Olfactory Mucosa & Info-chemical Communication

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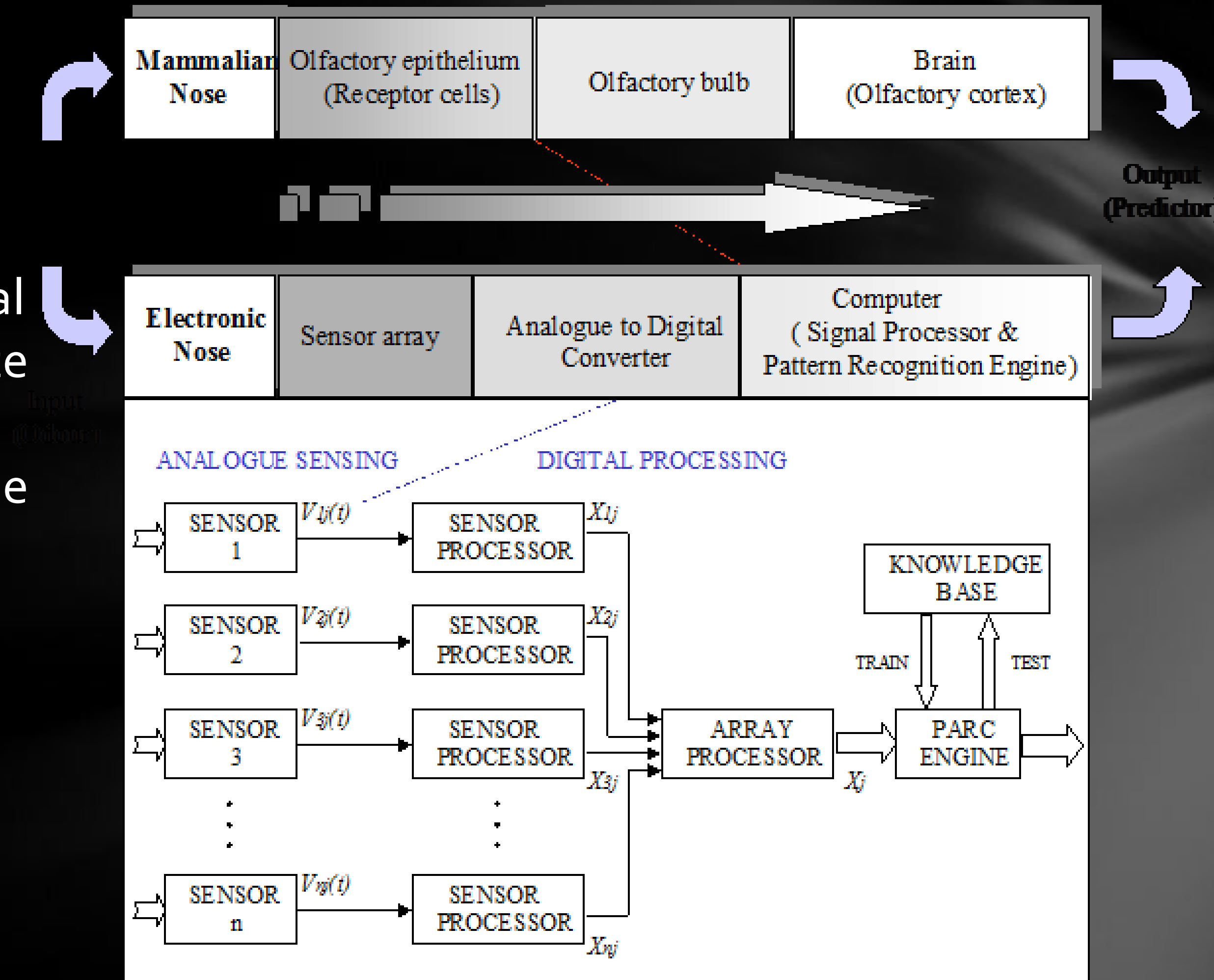
Sensor Array based E-noses

"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"



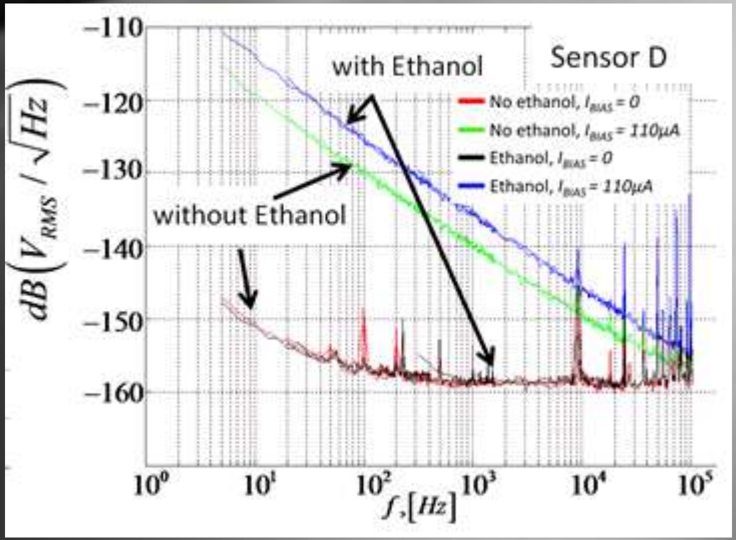
Source: Gardner & Bartlett
Sens. Actuators 18 (1994) 211

Chemical sensors suffer from noise

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

Examples:

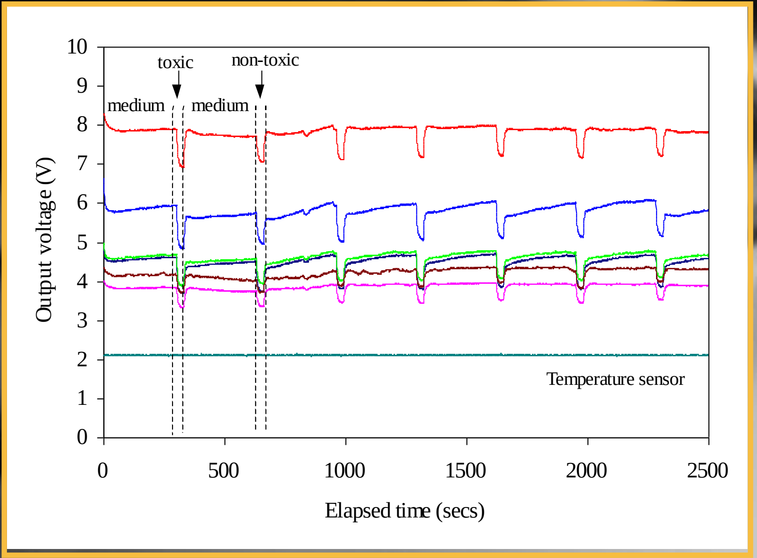
- Johnson noise, Shot noise, flicker noise
- Sample errors
- Digital bit error
- Chemical noise is often 1/f noise
- Parameter S/N



Source: Falconi et al. Sens. Actuators B (2012) at press

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)

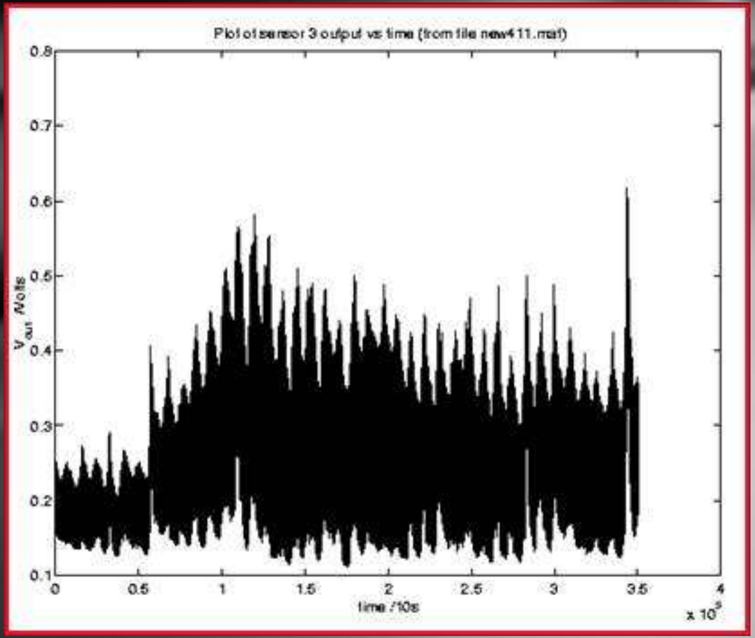
Source: Searle et al. 2002 *IEEE Sensors Journal* 2 218

Chemical sensors suffer from drift

Variation over time of signals and parameters

Examples:

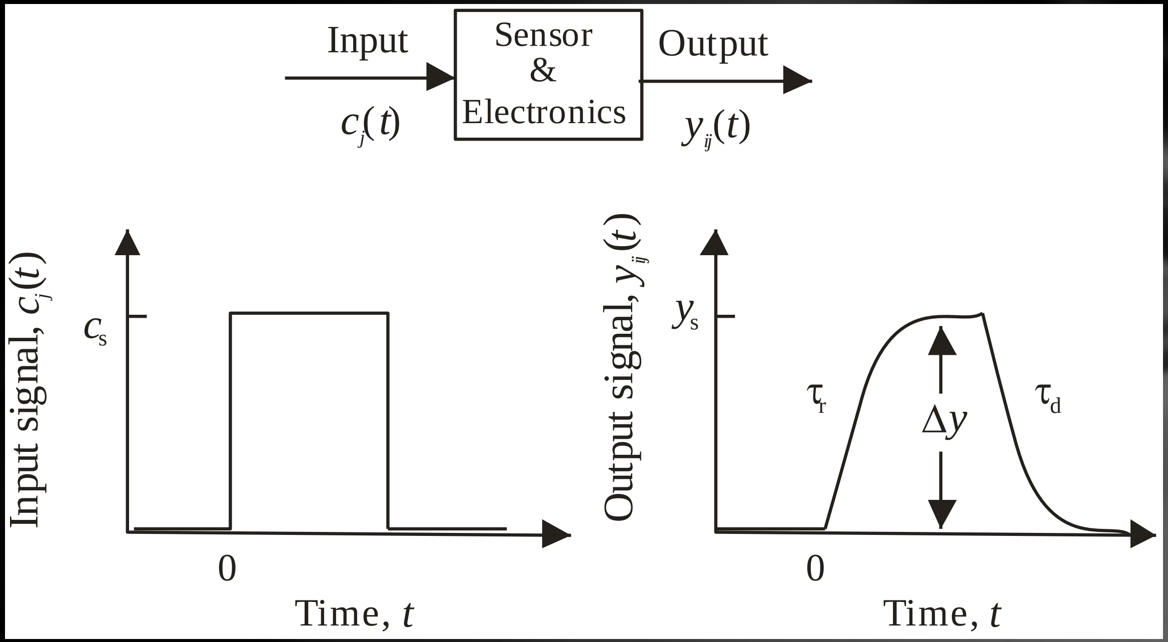
- Aging of sample
- Baseline or response of sensor
- Parametric drift
- Aging of sensor material
- Poisoning of sensor
- Parameter: dS/dt



Source: Searle et al. 2002 *IEEE Sensors Journal* 2 218

Pre-processing algorithms help …

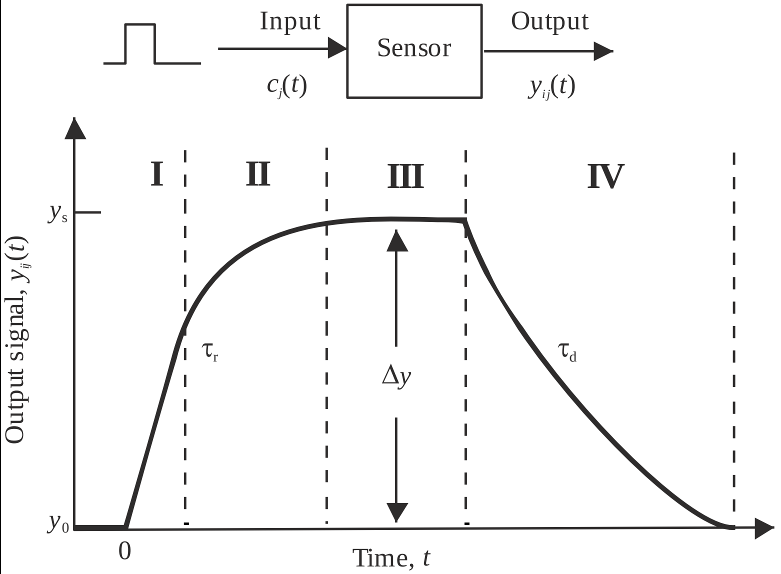
Feature selection:

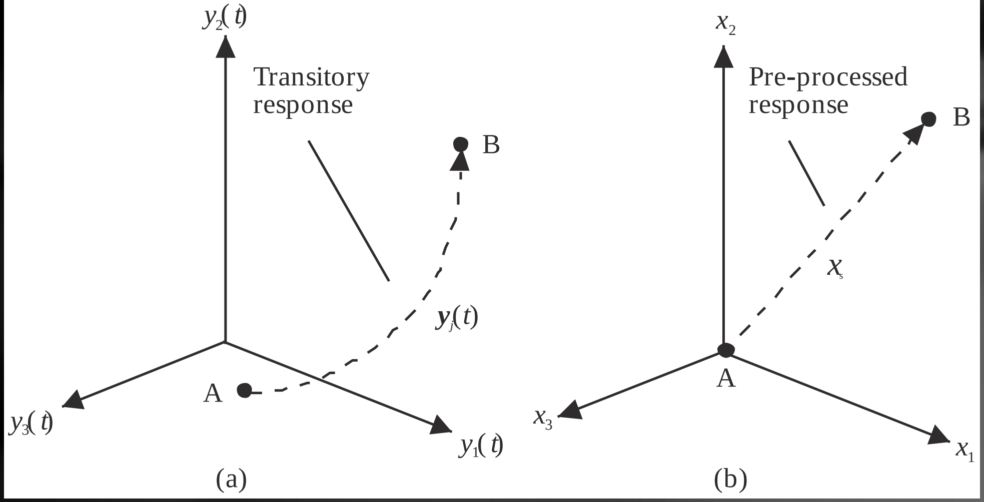


- For additive interferences use <u>differential</u> signal (S_2-S_1)
- For multiplicative interferences use signal <u>ratio</u> S_2/S_1

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 ….

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

Source: Pearce et al (2003) *Handbook of Machine Olfaction*, Wiley-VCH, Dordrecht, pp592. ISBN 3-527-30358-8.

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)

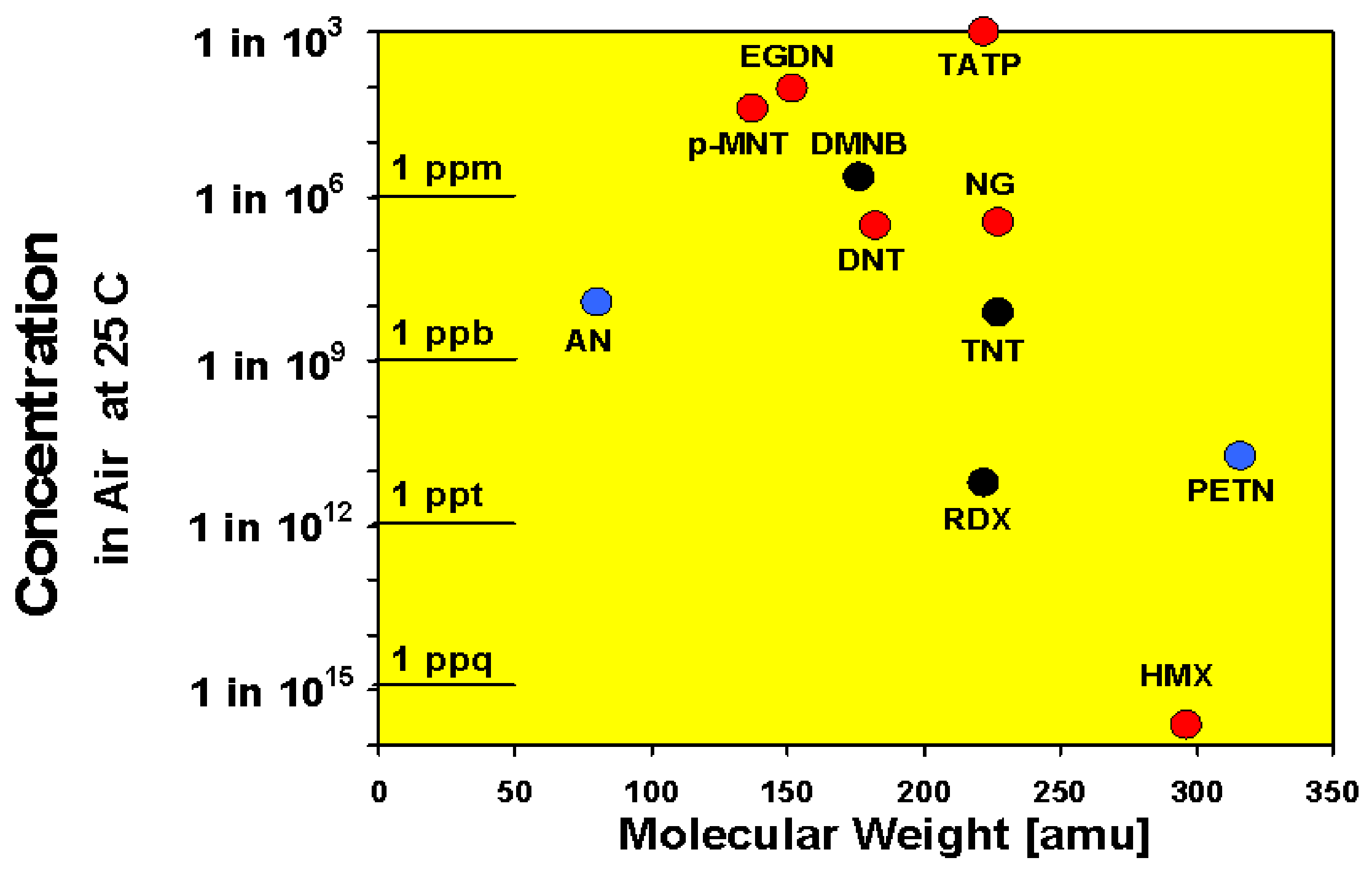
Detection of underground mines

- 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)

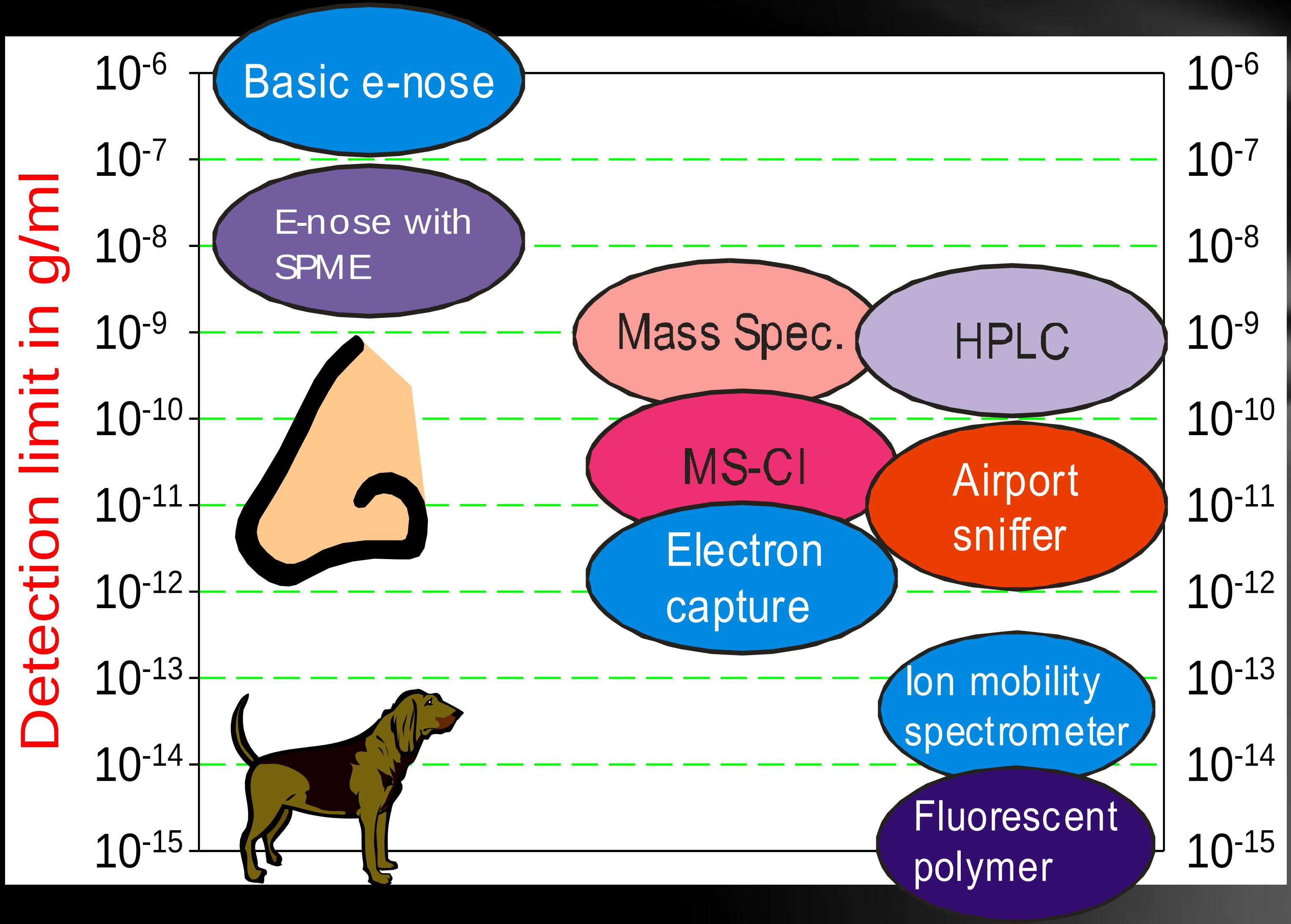
Trace level explosive materials



Source: **Gardner JW** in *Electronic Noses & Sensors for the Detection of Explosives* (Eds **JW Gardner** and J Yinon), NATO Science Series II Mathematics, Physics and Chemistry – Vol.159, Kluwer, Dordrecht, 2004, pp.1-28, ISBN 1-4020-2317-0 & ISBN 1-4020-2318-9.

Humidity mg/ml

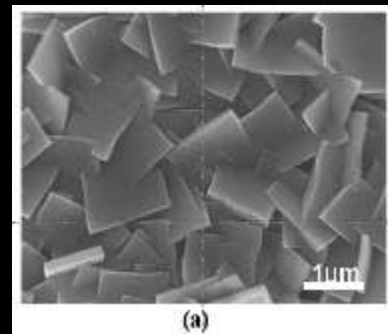
EUNetAir – Low cost please?

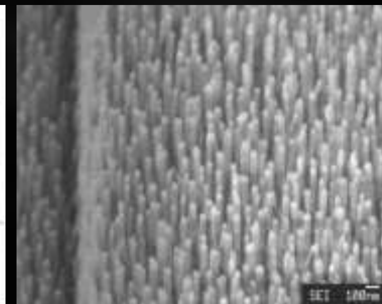
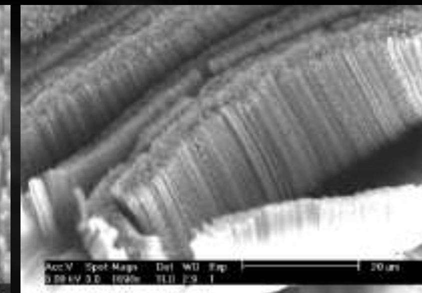


New Approaches: Gas/Odour Microsensors

Nanomaterials

- Metal oxides
- CNTs
- Polymers

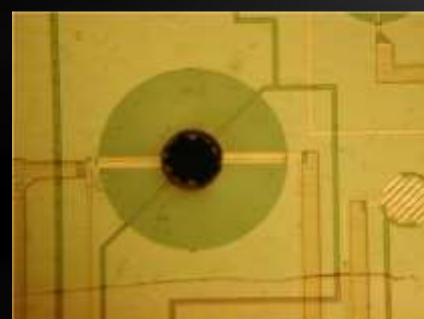
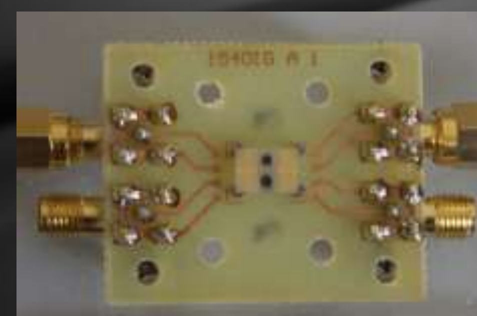


Source: Santra et al 2010 *Sensors and Actuators B* **146** 559

CMOS gas sensors

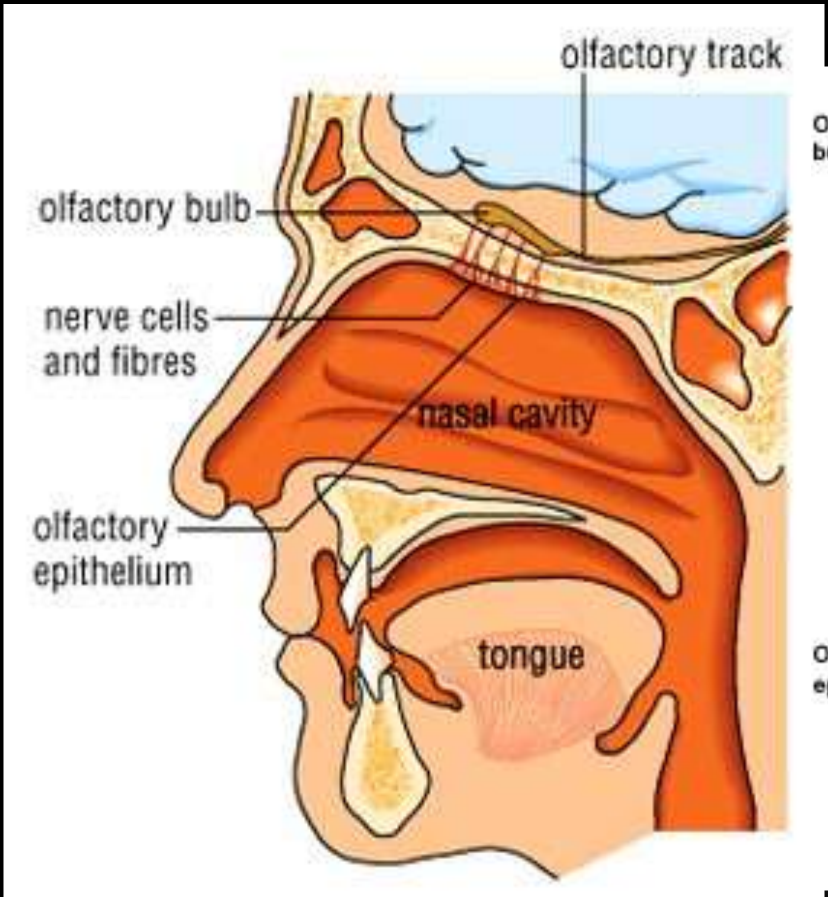
- Resistive
- Calorimetric
- Thermal modulation

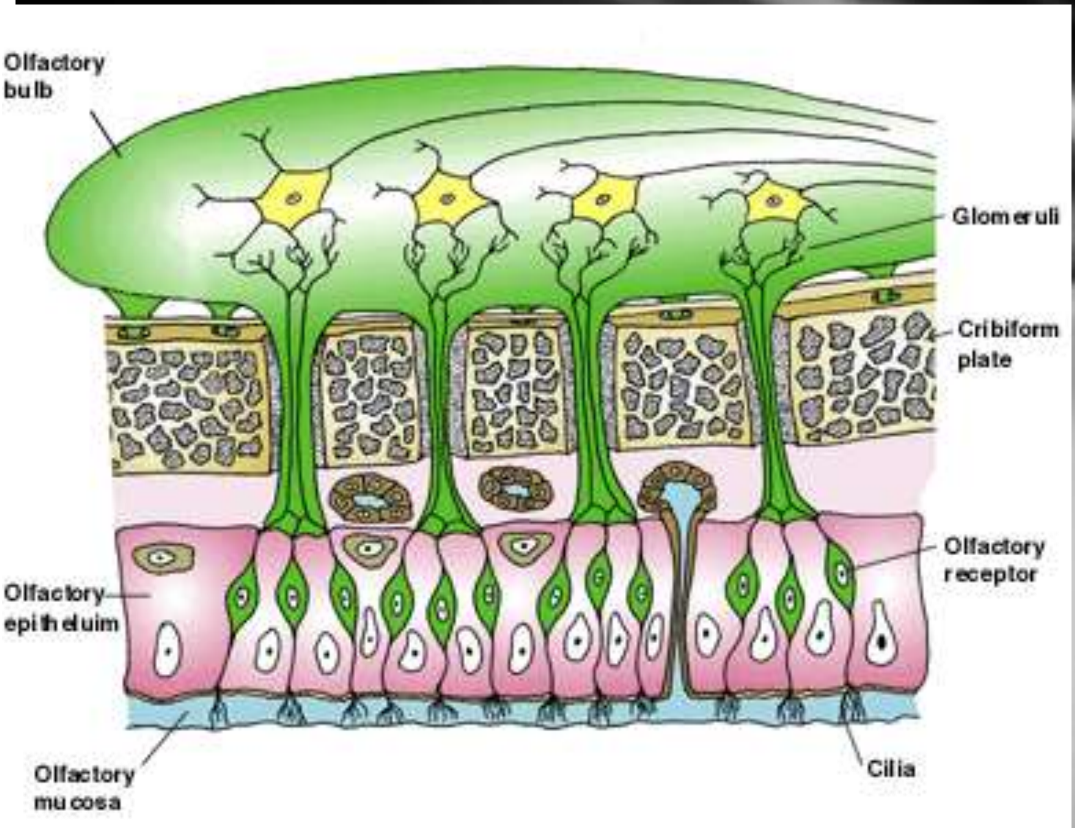



Source:
Santra et al 2010 *Nanotechnology* **21** 1
Iwaki et al 2009 *IEEE Sensors Journal* **9** 314

Artificial e-mucosa and Ratiometric chemoreception

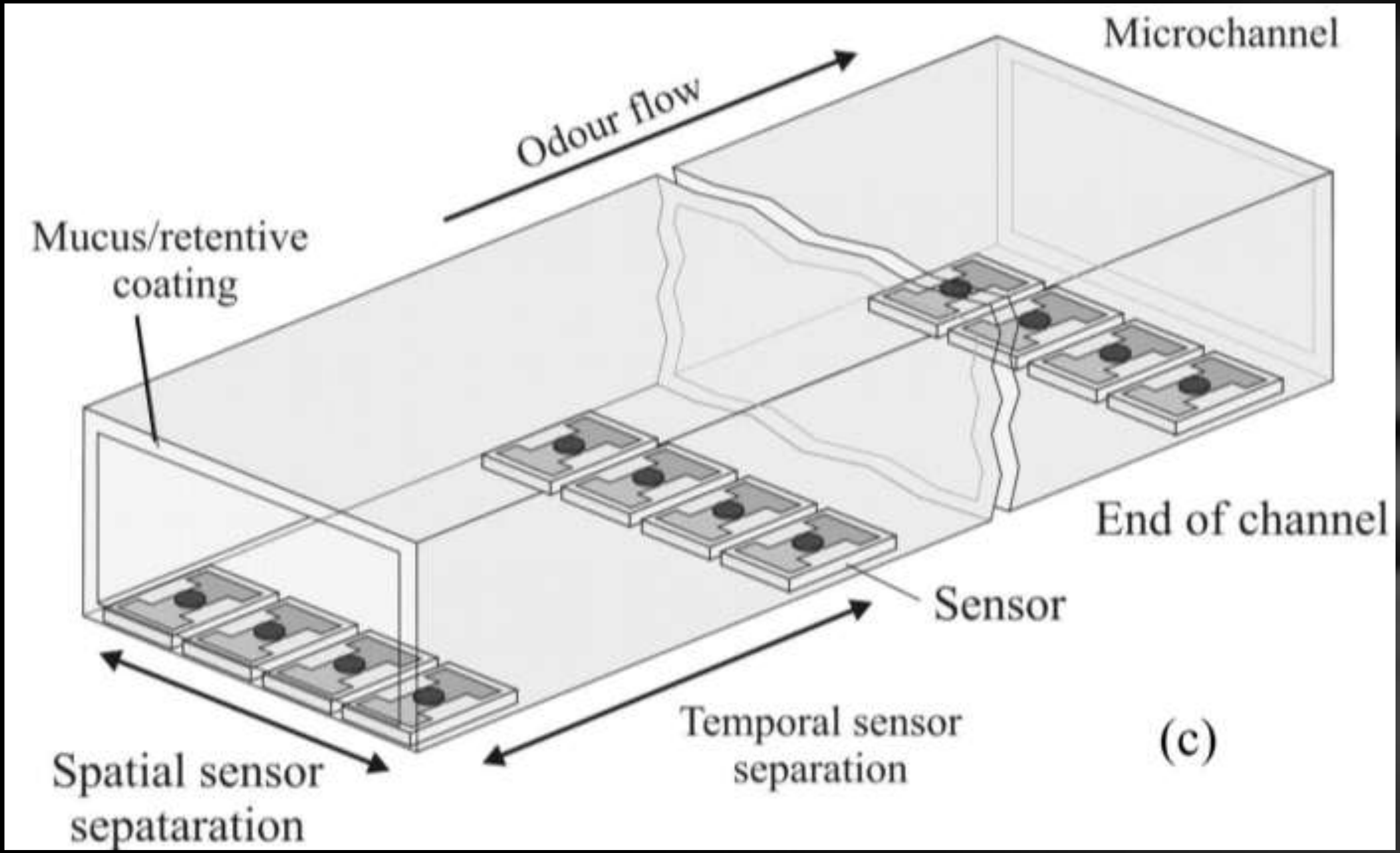
Human Olfactory Mucosa





Distributed array of olfactory cells along mucous coated nasal cavity

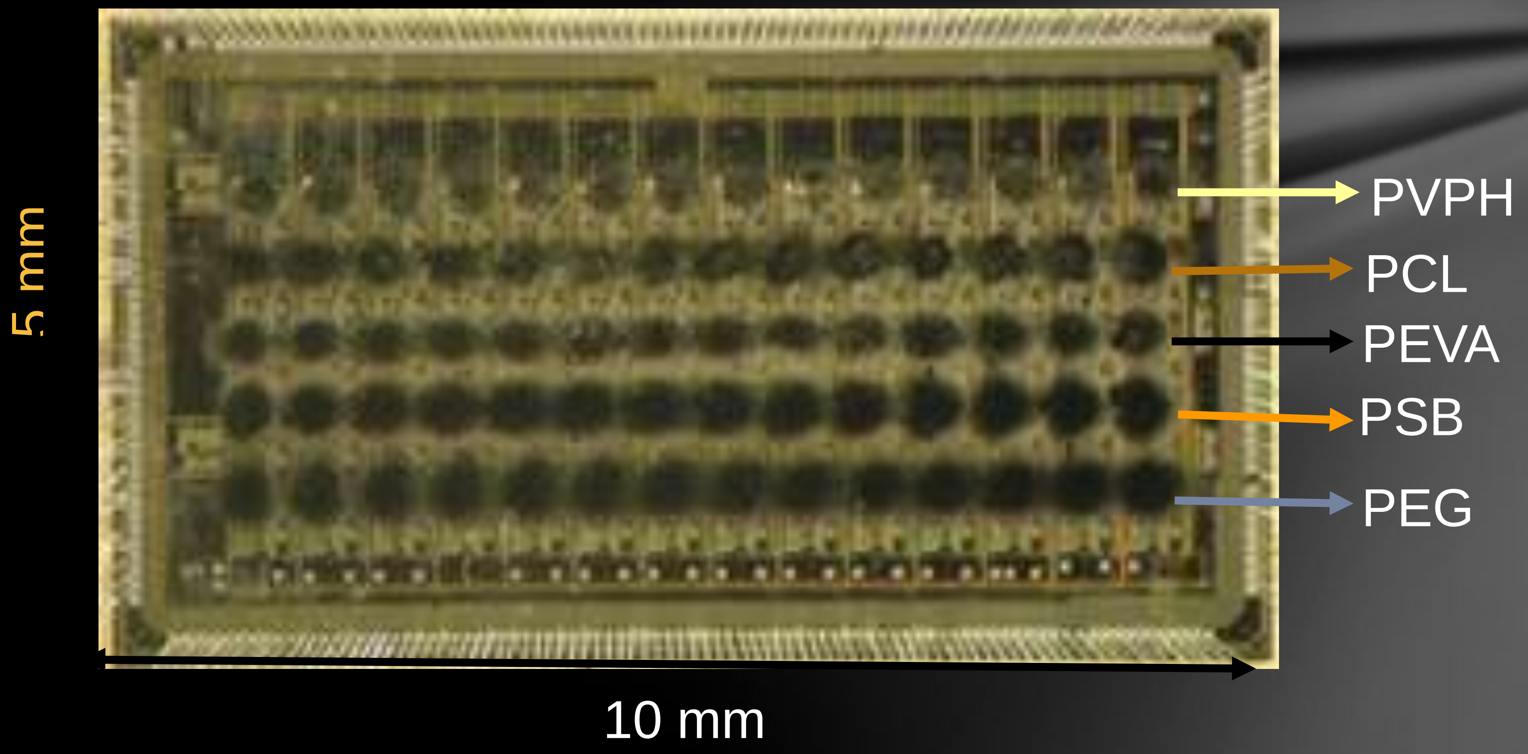
Warwick E-mucosa



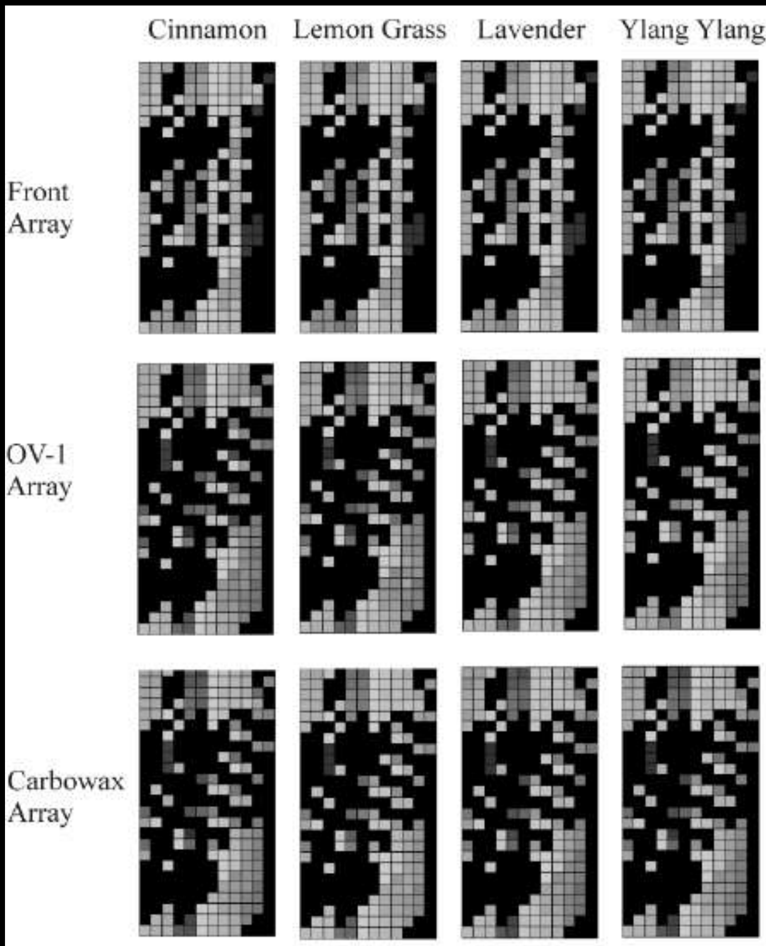
Source: Sanchez-Montanes et al 2008 *Proc. Roy. Soc. A*, **464**

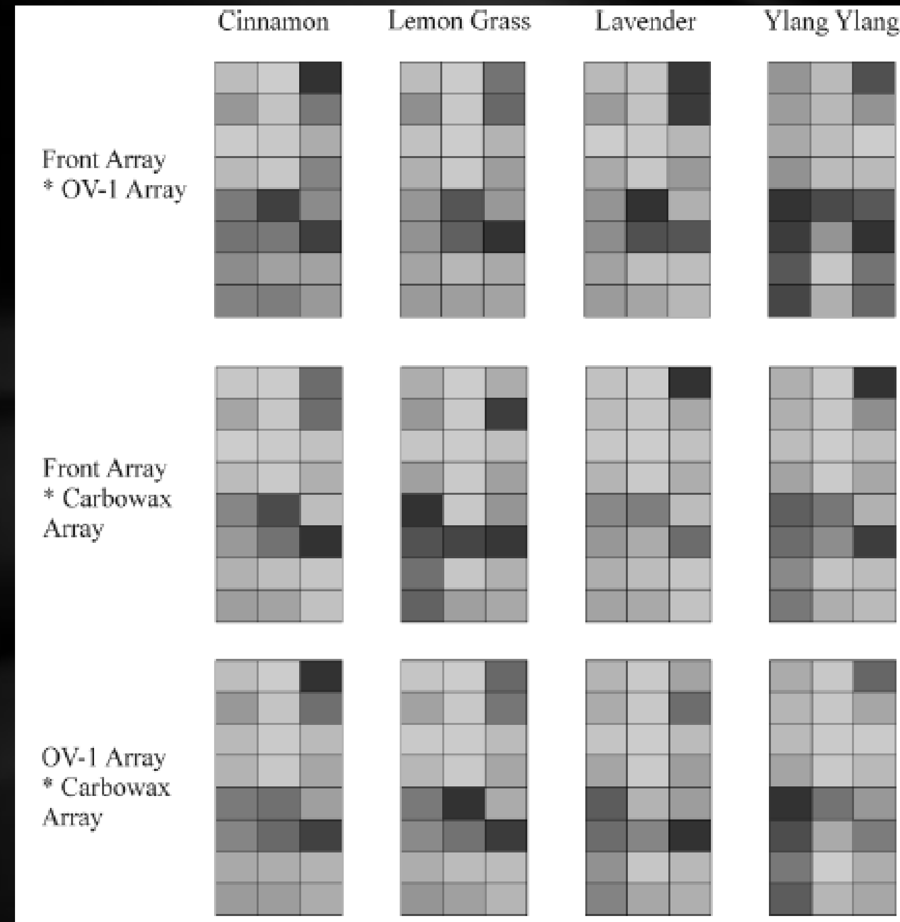
Large CMOS sensor arrays

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



25 x 12 Sensor Array Response to Oils – Convolution between front and back arrays





Gardner JW et al 2009 *IEEE Sensors Journal* **9** 929

$$y(t) = \int_{\tau=-\infty}^{\infty} S_B(\tau) S_A(t-\tau) d\tau .$$

No baseline signal used

INSECT-BASED INFO-CHEMICAL COMMUNICATION SYSTEM (iCHEM)

Information Society Technologies

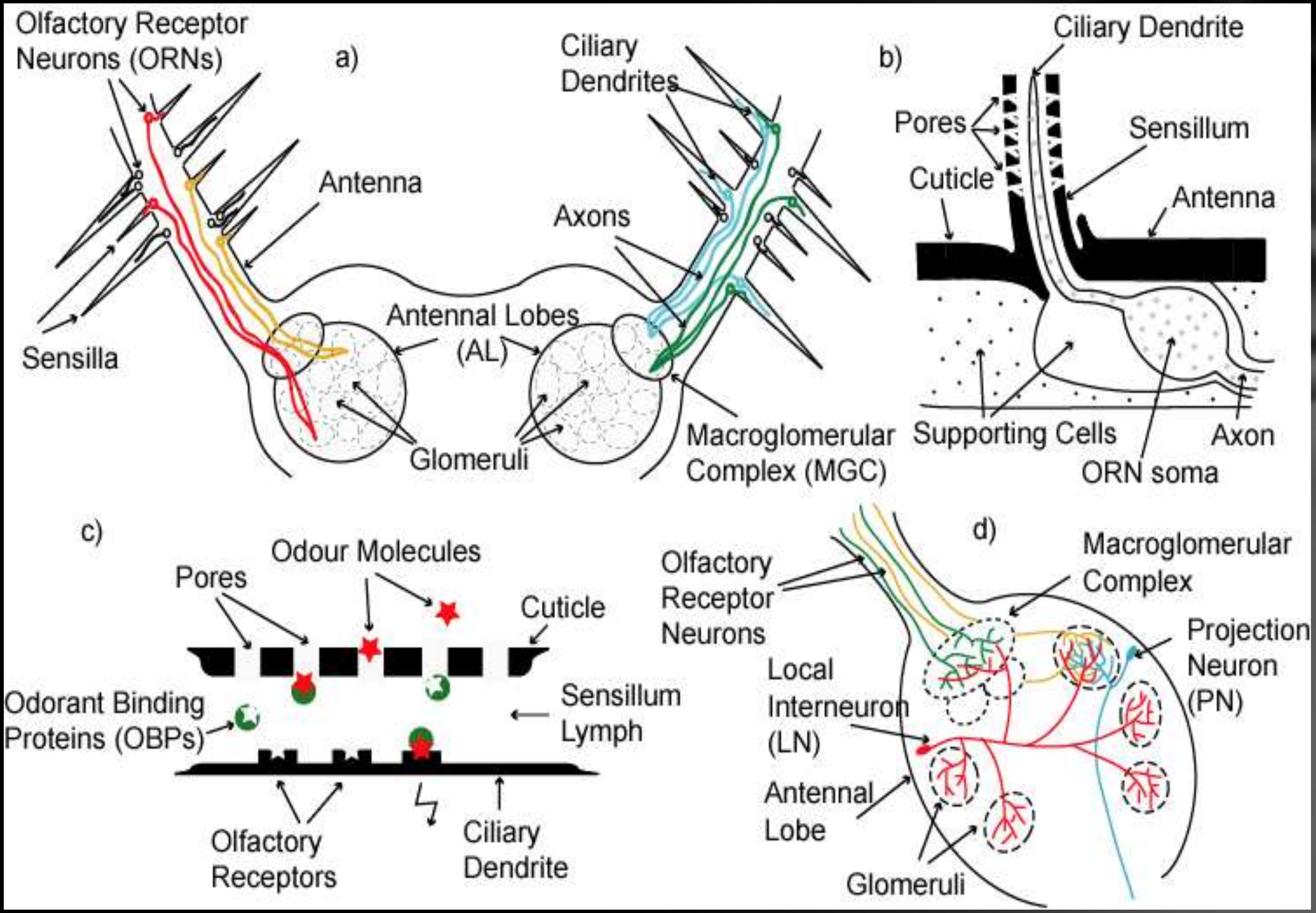
THE UNIVERSITY OF WARWICK

University of Leicester

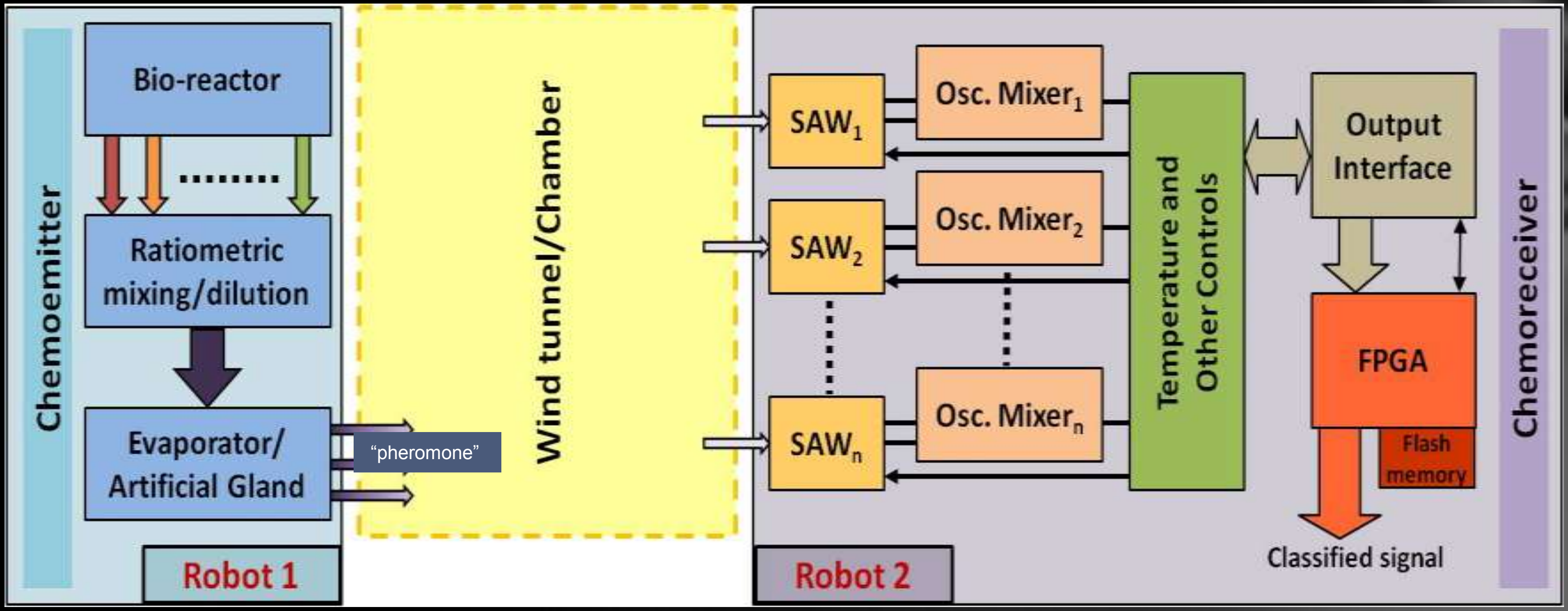
MPI-BGC Jena

MESA+ Institute for Nanotechnology

Insect-Based Chemoreception



Ratiometric detection of molecules



Source: Cole et al 2009 *Proceedings of IEEE Sensors Conference*, 978-1-4244-5335-1/09

Example: Fruit volatiles

	Chemical	GC (%)
Apple 	butyl hexanoate	37
	pentyl hexanoate	5
	propyl hexanoate	4
	butyl butanoate	10
	hexyl butanoate	44
	butyl hexanoate	0.01
Hawthorn 	3-methylbutan-1-ol	4
	isoamyl acetate	1.5
	4,8-dimethyl-1,3(*E*),7-nonatriene	0.09
	ethyl acetate	94.3
	dihydro-β-ionone	0.10
	β-caryophyllene	5.8
Dogwood 	3-methylbutan-1-ol	27.5
	isoamyl acetate	0.9
	1-octen-3-ol	9
	ethyl acetate	54.9
	dimethyl trisulfide	1.9

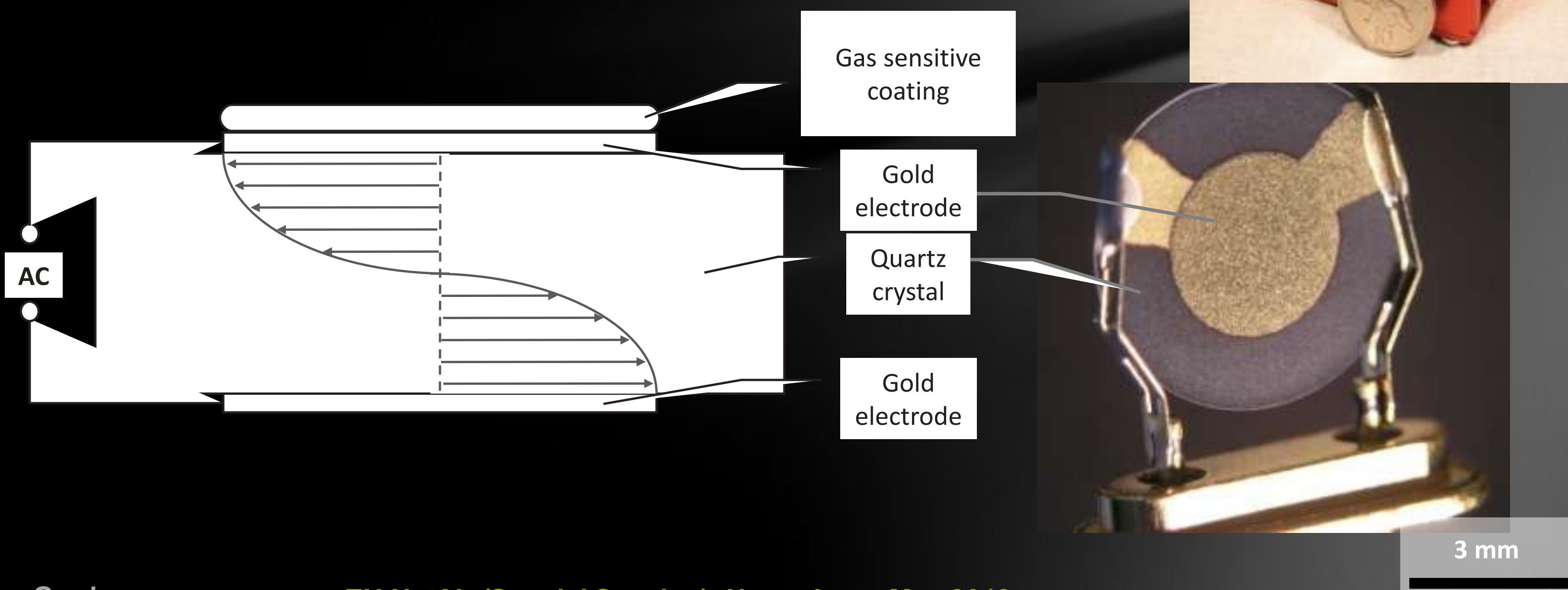
(Linn et. al, 2005)

Quartz Crystal Microbalance (QCM)

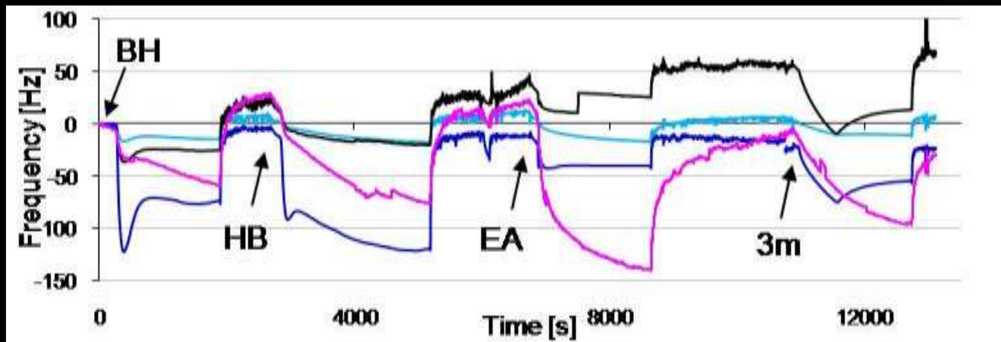
Operational Mechanism: Sauerbrey equation

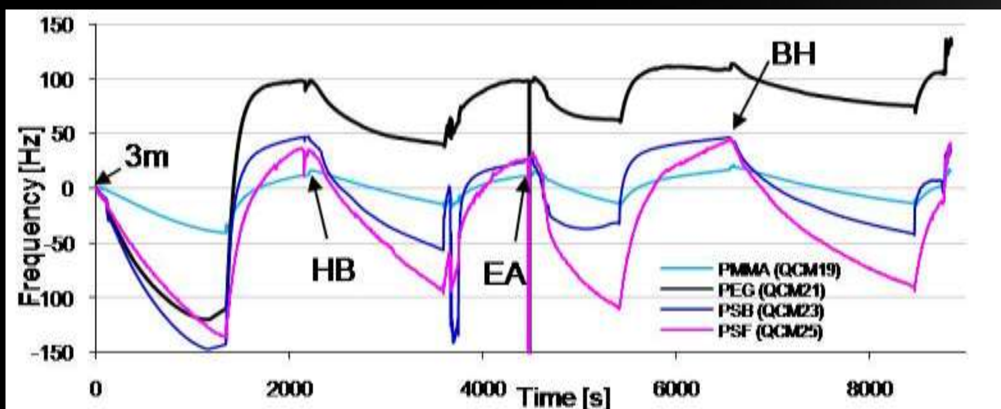
$$\Delta f = -\frac{2 f_0^{\,2}}{A\sqrt{\rho_q \mu_q}} m_f$$

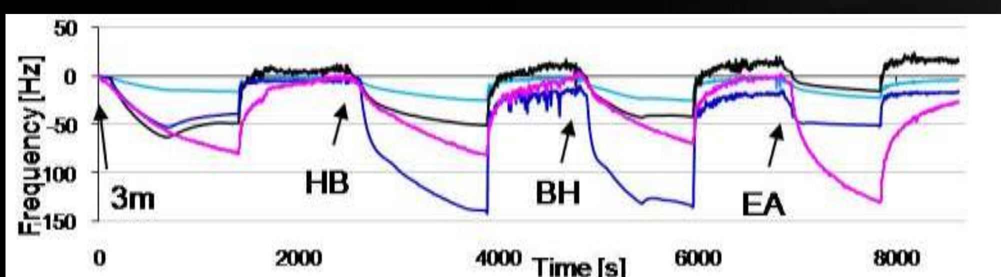
Sensitivity: *Δf = 7.2 Hz/ng*



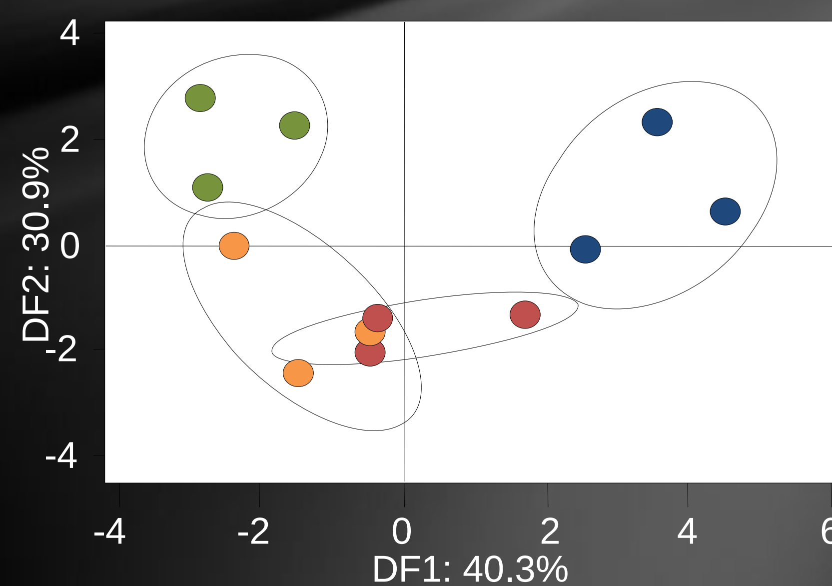
Ligand detection using QCMs



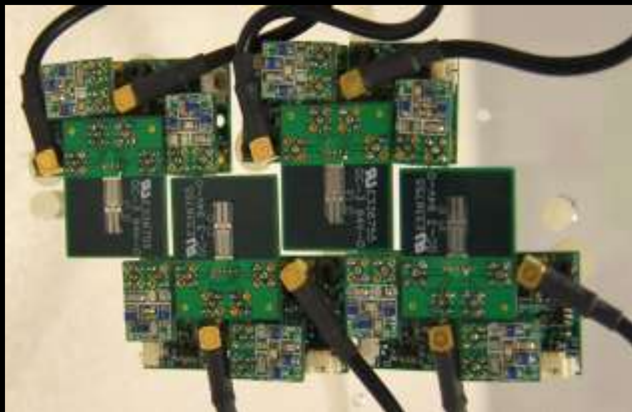


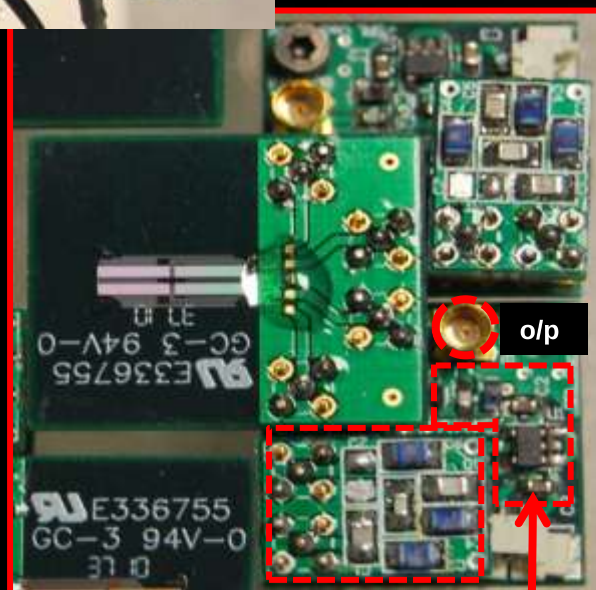


	Odorant	PSF	PSB	PEG	PMMA
1. seq.	3m	137	144	110	42
	HB	127	103	58	29
	EA	136	57	35	28
	BH	134	87	33	32
2. seq.	BH	59	77	26	15
	HB	98	127	31	14
	EA	157	28	59	26
	3m	90	39	46	18
3. seq.	3m	80	39	49	16
	HB	82	138	57	24
	BH	69	118	53	22
	EA	130	33	31	22



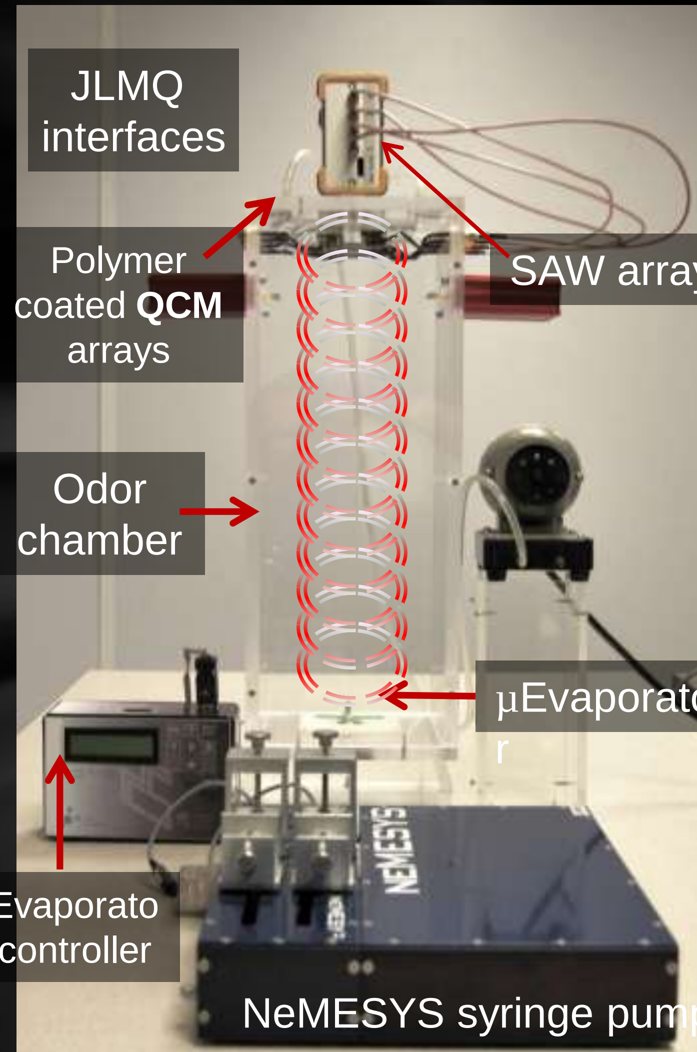
Ratiometric Compounds: Quad Array of Dual 262 MHz SAWR





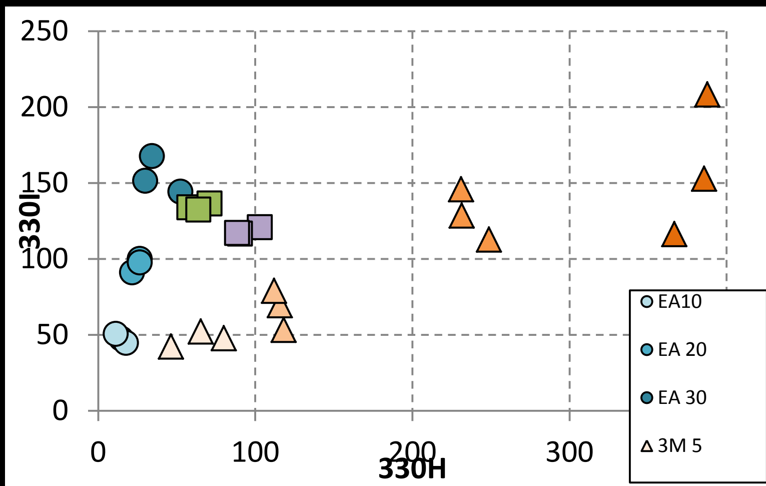
Filter Board

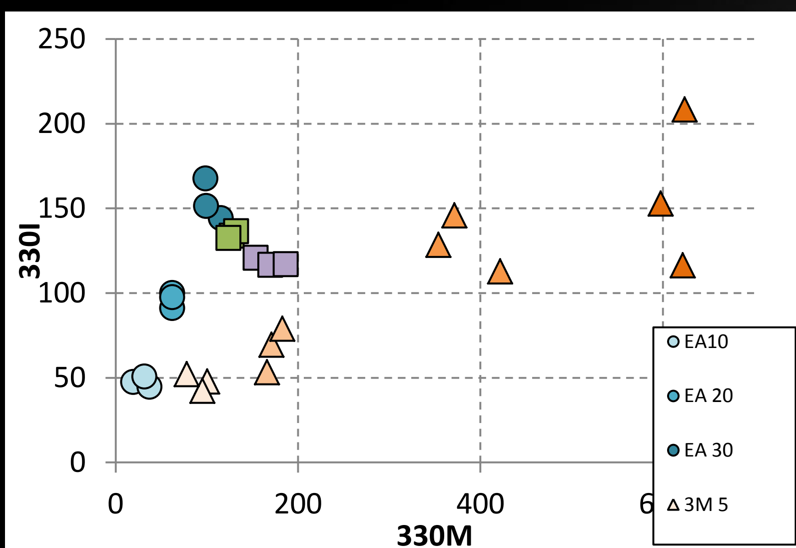
Oscillat or circuitry

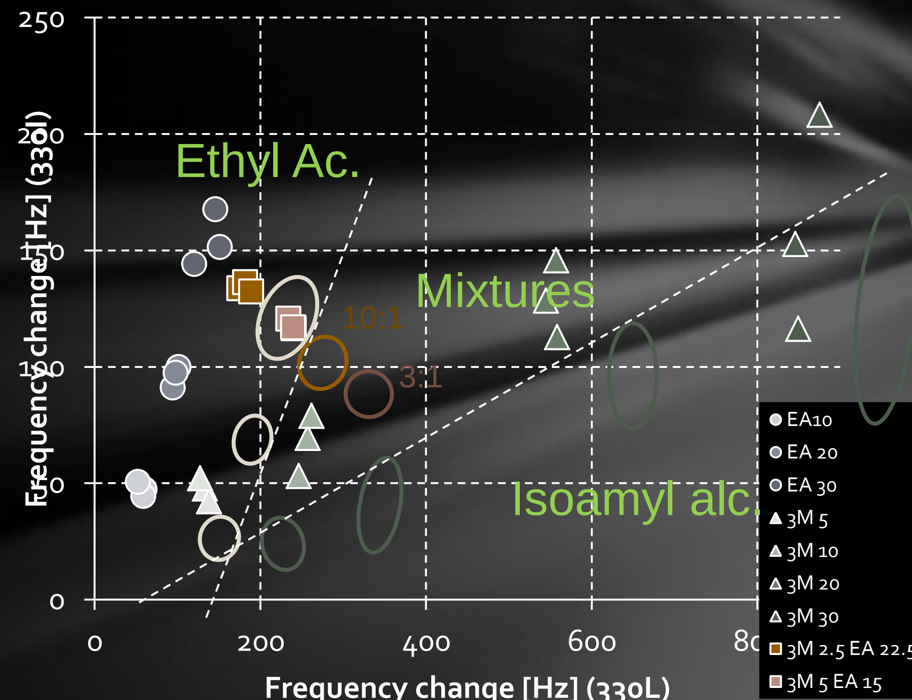


Liquid phase: Leonte et al 2006 *Sens. Actuators B*, **118**, 349
Pheromones in air: Poster P2.2.12 Thomas et al. IMCS 2012

Ratiometric decoding using sensor responses

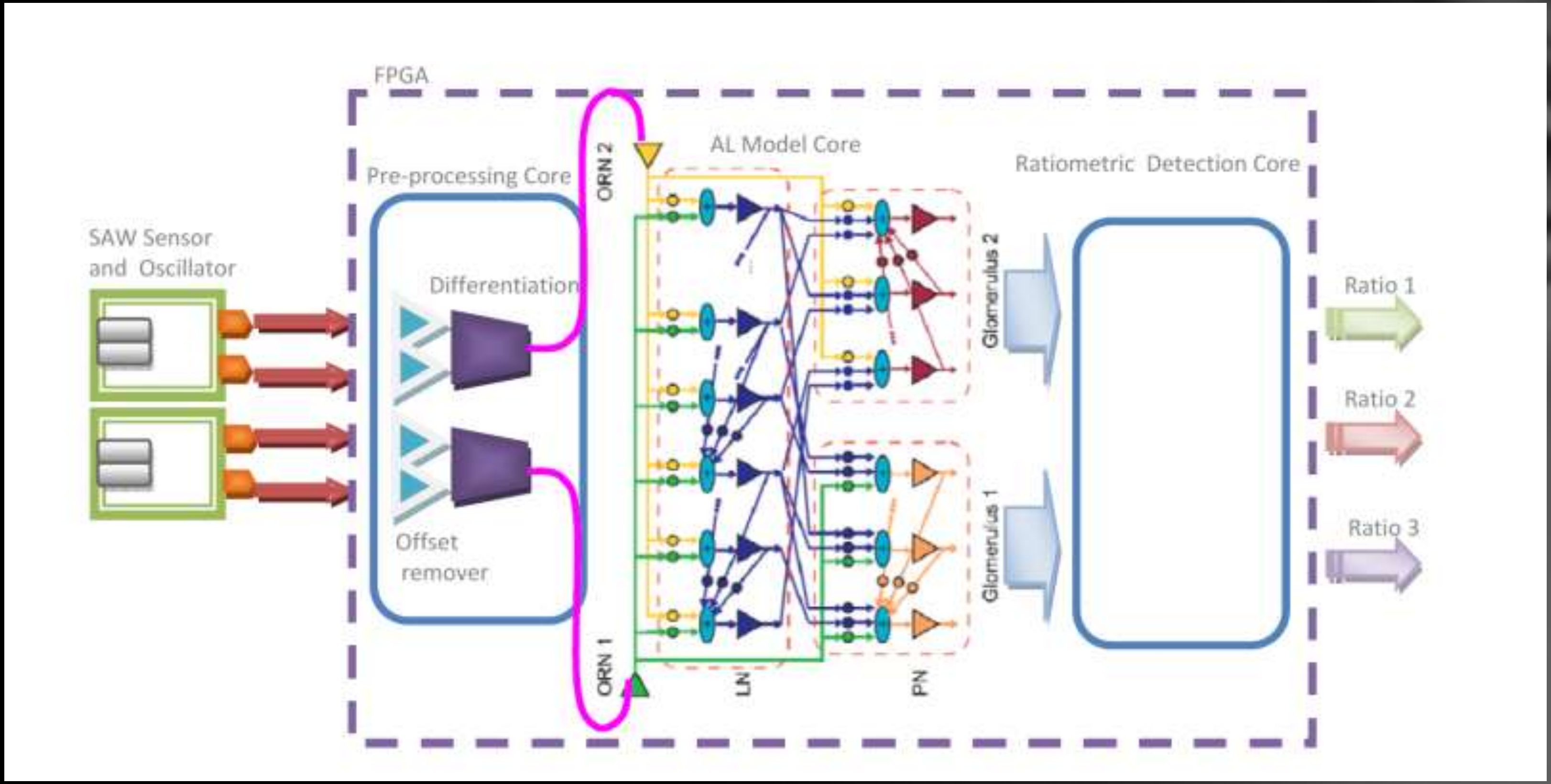






Source: Sensors and Actuators at press

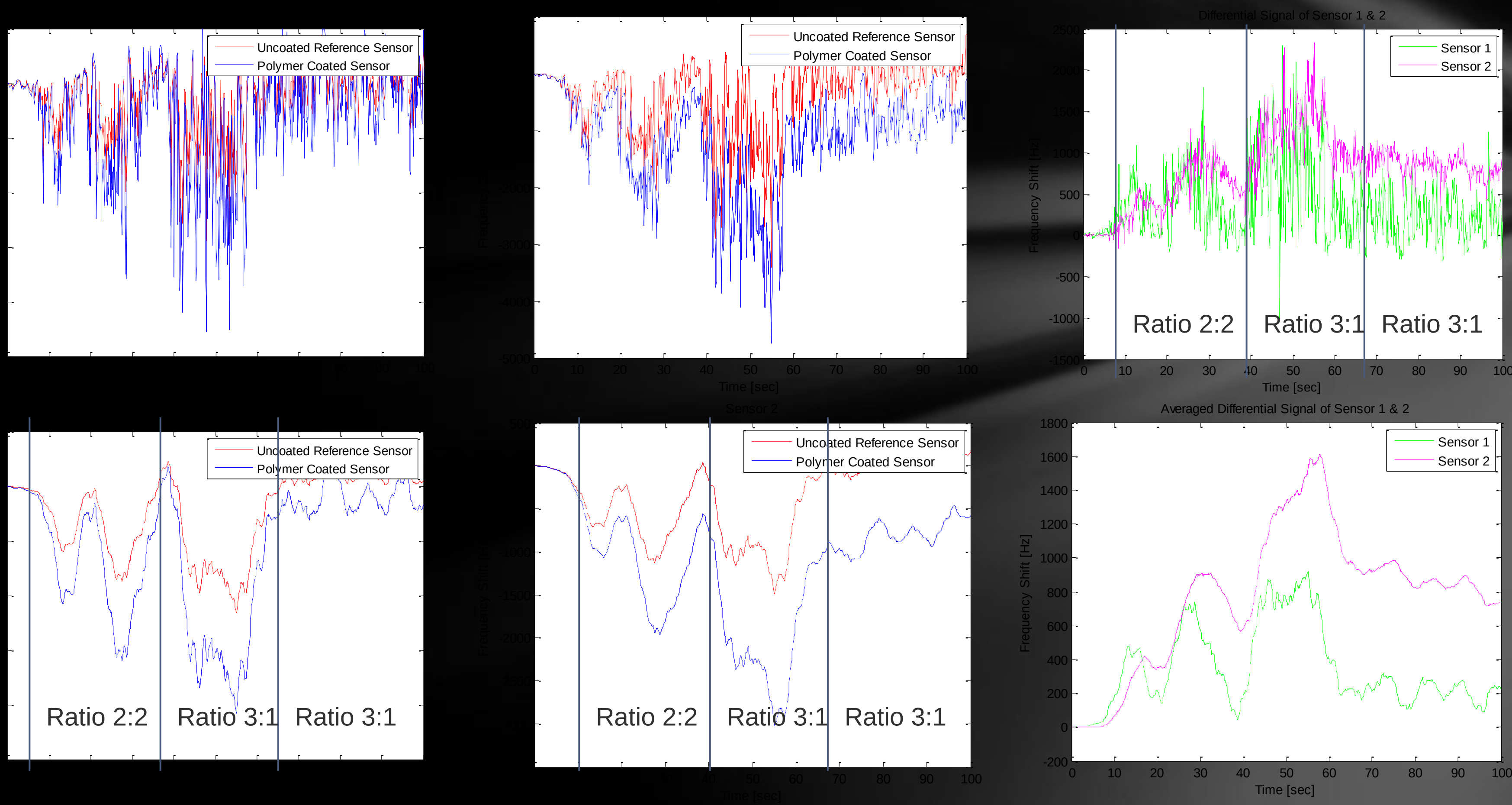
Neuromorphic FPGA of Insect Antennal Lobe



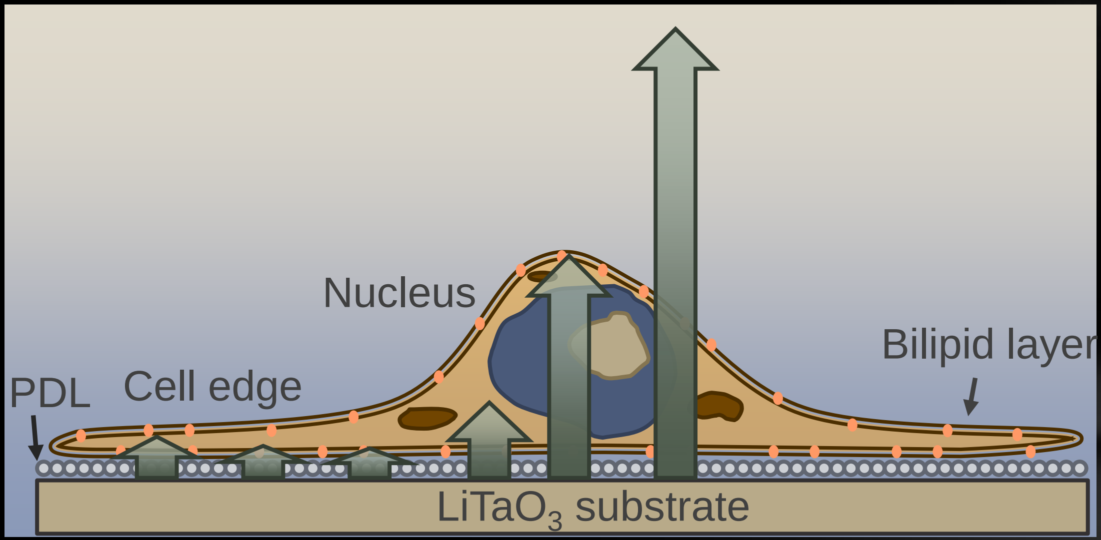
Source: Racz et al Int J Circuit Theory and Applications 2012 at press

Real-time Chemical Communication

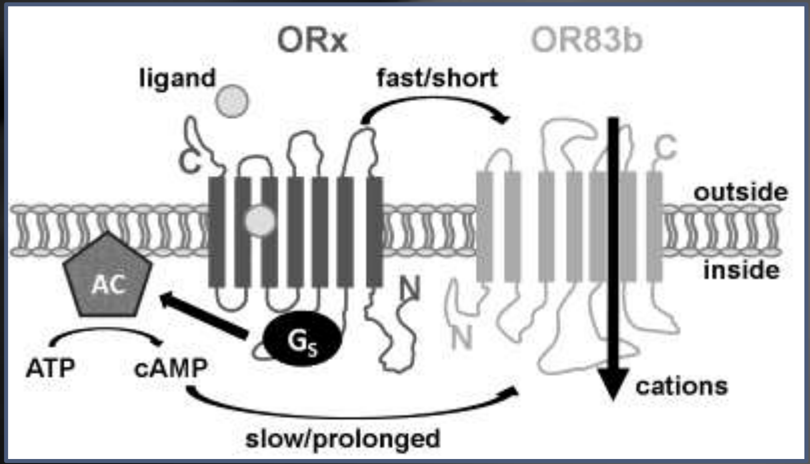
http://www.youtube.com/watch?v=lBLN3sCbbPY



Finally .. Cell-based Sensors

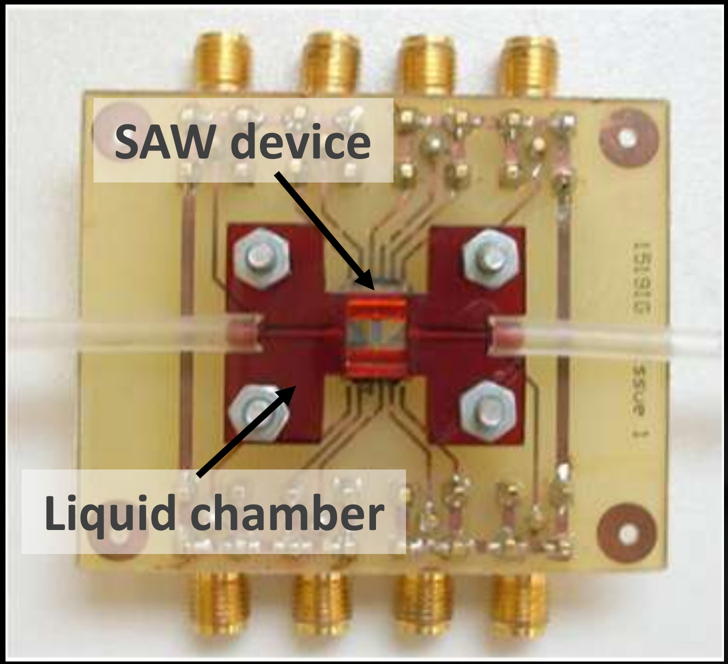


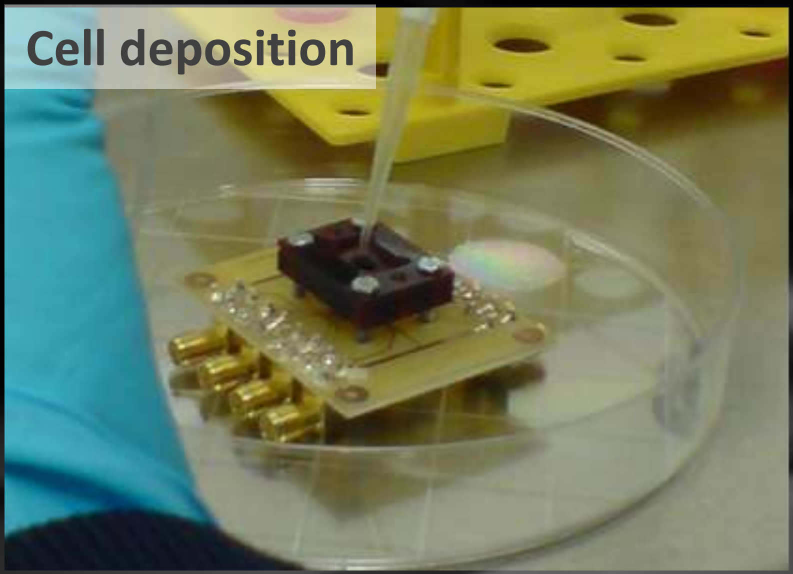
	Thickness [nm]	Frequency [MHz]	Feature size [nm]
Poly-D-lysine	15	39,901	26
Bilipid layer	22.5	26,600	39
Edge of cell	615	973	1,069
Middle of cell	7,515	80	13,064
Upright cell	15,015	40	26,102

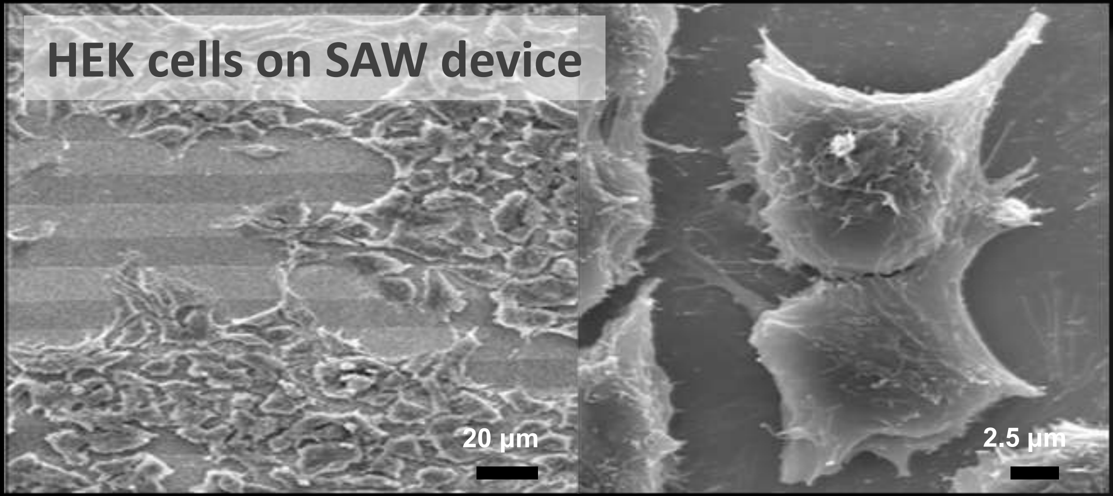


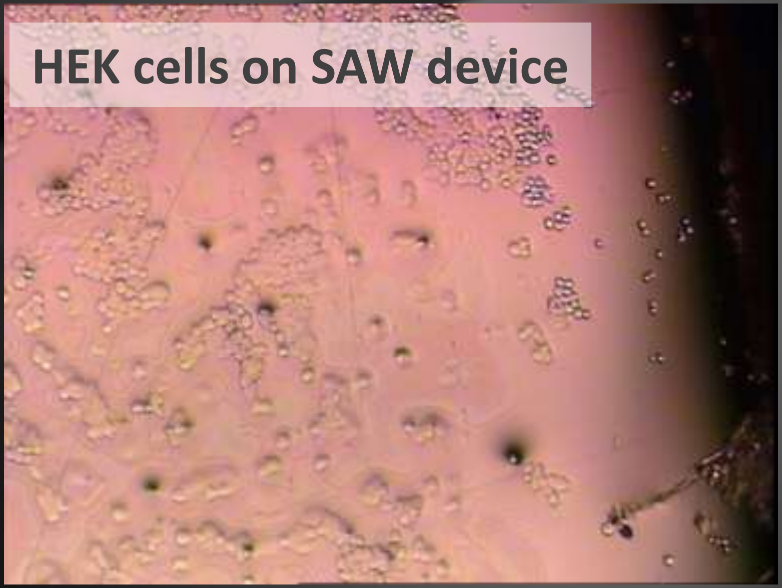
Source: Racz et al Int J Circuit Theory and Applications 2012 at press

Cell based SAW sensor for Ligands









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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

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