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

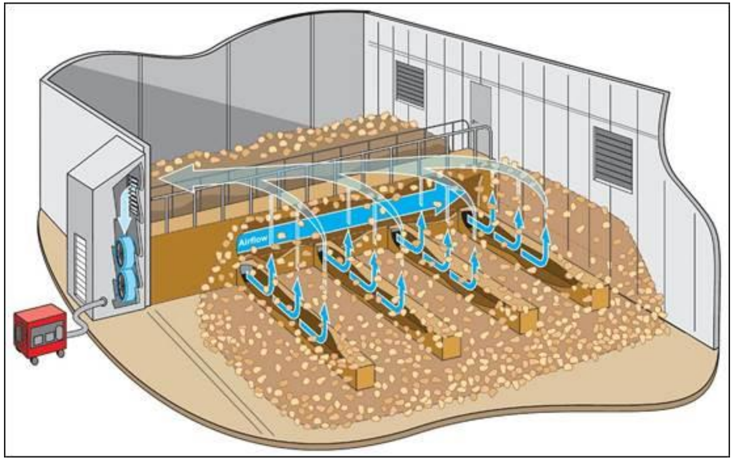
Members of the Tolsma-Grisnich Group

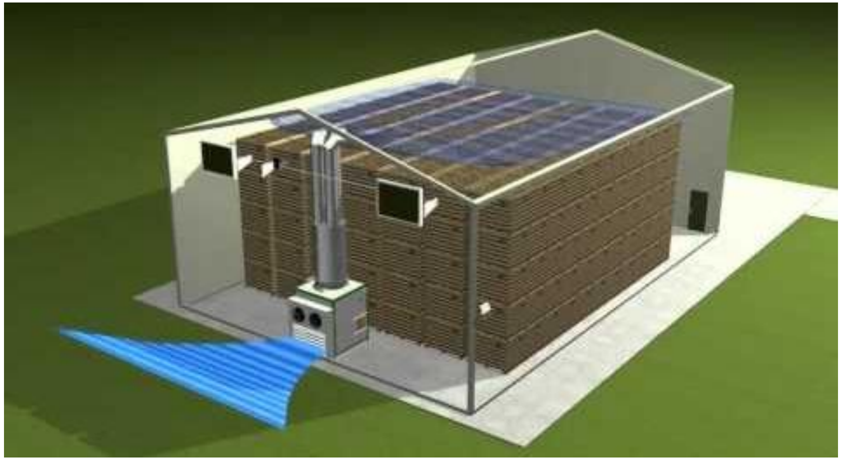
Partners

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)
- CO_2 is also monitored

30% losses without warehousing system

Big problem in e.g. developing world…

Potato Storage Systems

TECH FOR FUTURE
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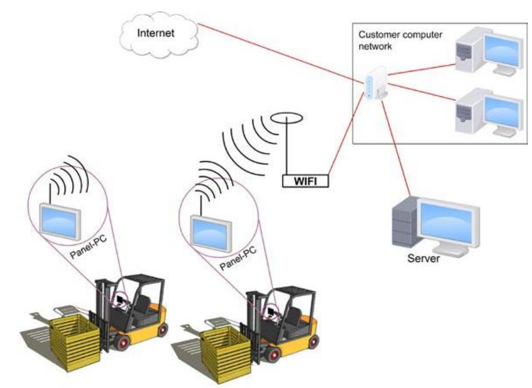
Multiple T and RH Sensors

Automatic Recipes

Energy Minimization

Can Track Batch from Field to Customer



Potato Storage Systems

TECH FOR FUTURE
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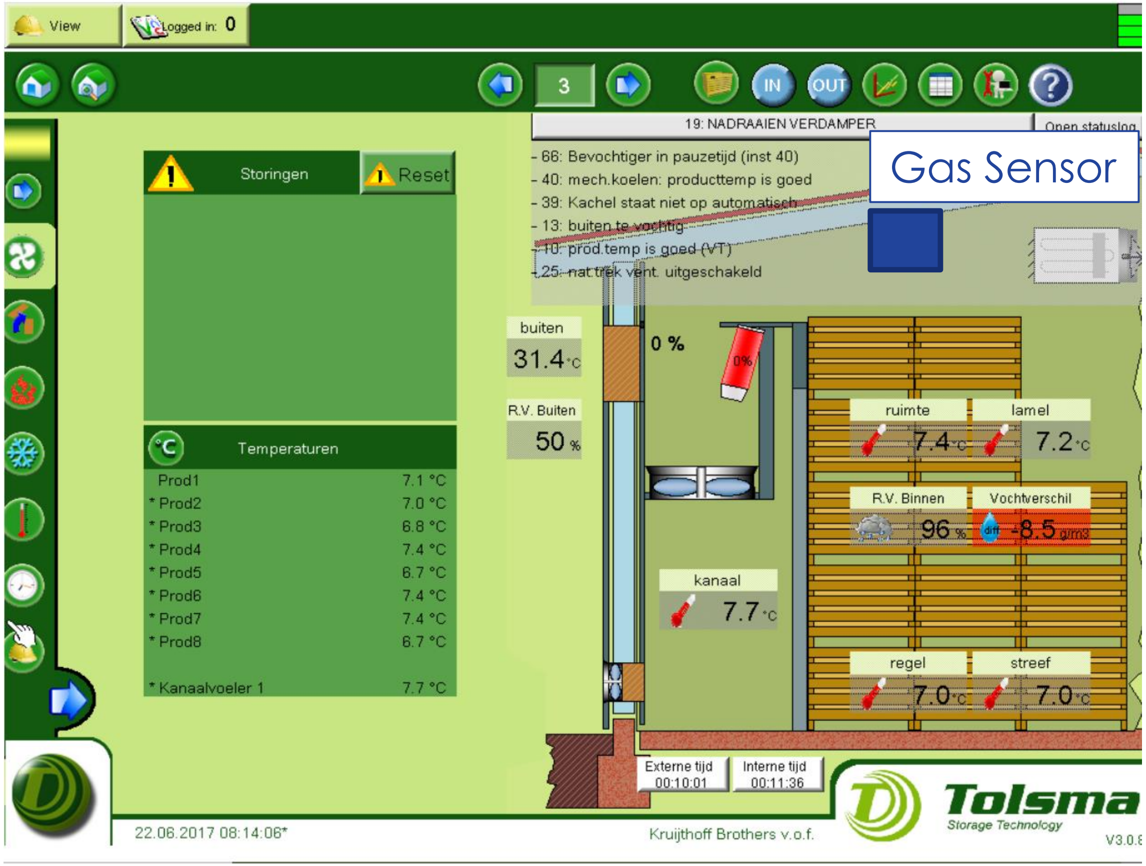


Add one more sensor

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

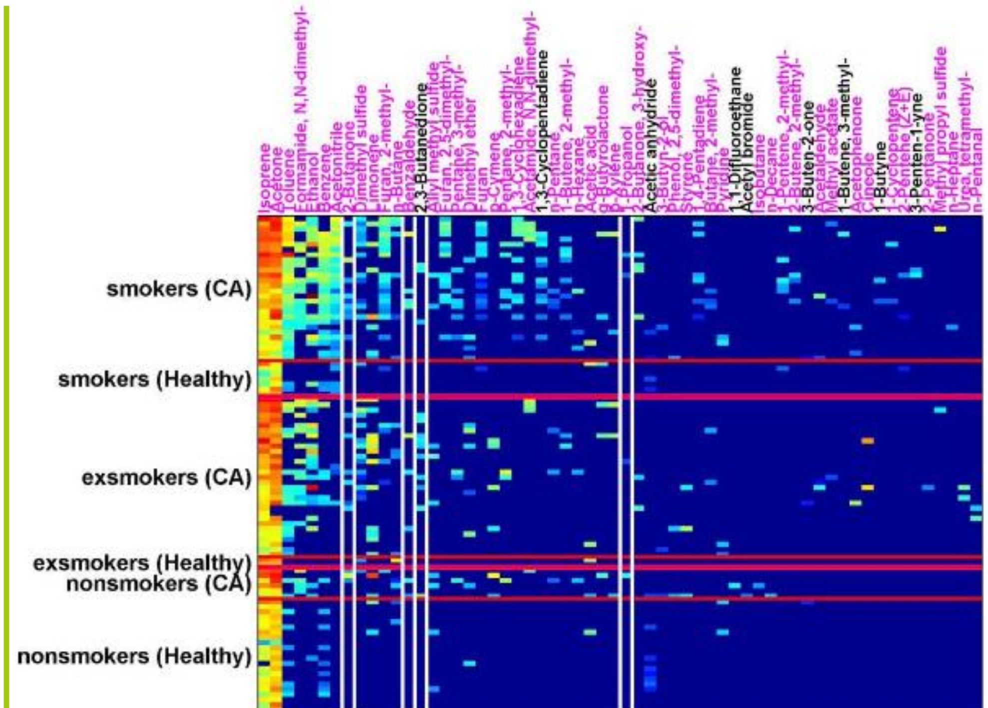
Challenges (specs):

- Ppm detection limit
- T and RH compensated
- Position, sampling?

Types of Gas Detection Principles

Analytical:
direct molecule detection

Chromatography
Spectrometry
…



Two mass spectrometry methods.

ΔConcentrations in ppb!

Not easy to separate CA from other diseases and carcinomas.

Noninvasive detection of lung cancer by analysis of exhaled breath
Batajevic et al.
BMC Cancer 2009 **9**:348

Types of Gas Detection Principles

TECH FOR FUTURE
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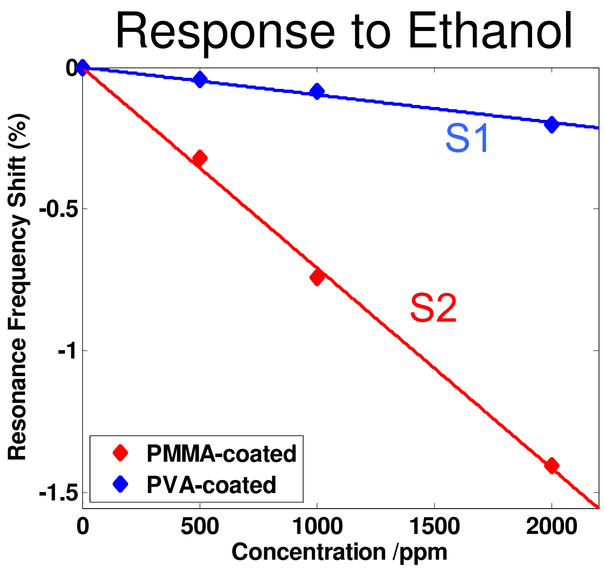
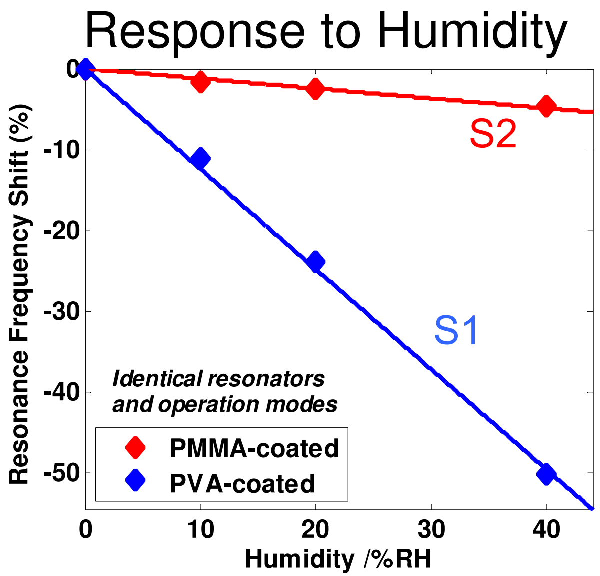
Analytical:
direct molecule detection

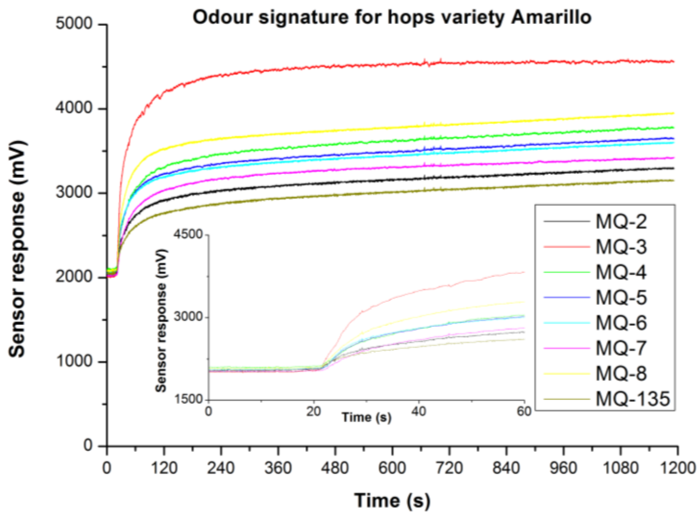
Chromatography
Spectrometry
…

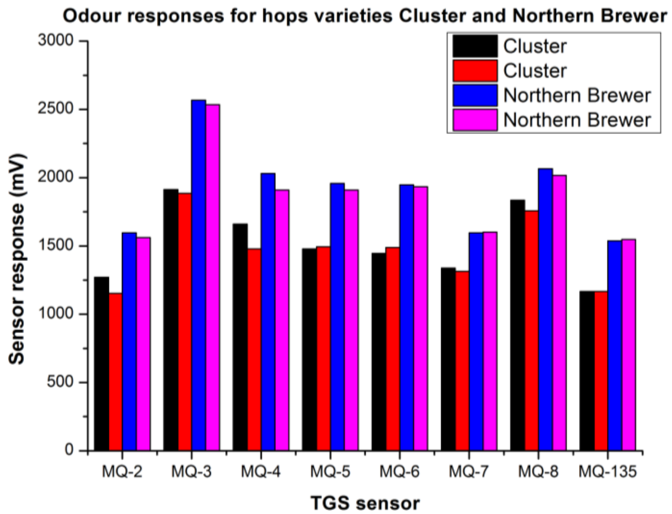
Semi-Analytical: Inverse Mixing Models
(only for known few-component compositions)

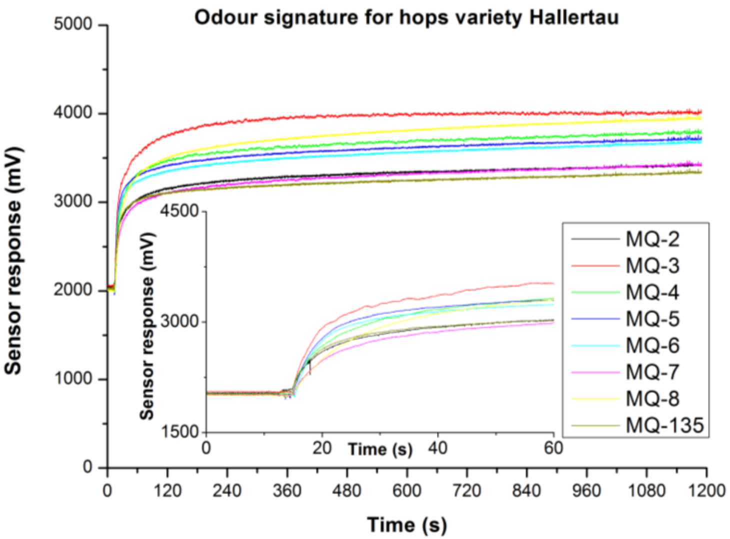


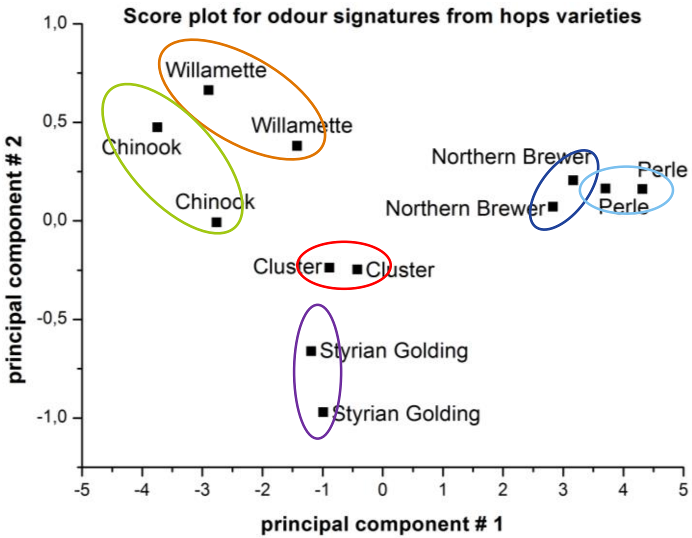


TWO SENSORS $S1 \neq S2$









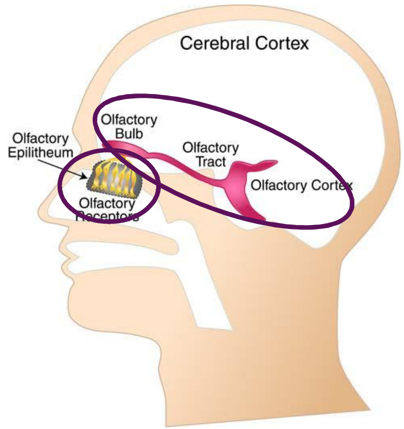
Types of Gas Detection Principles

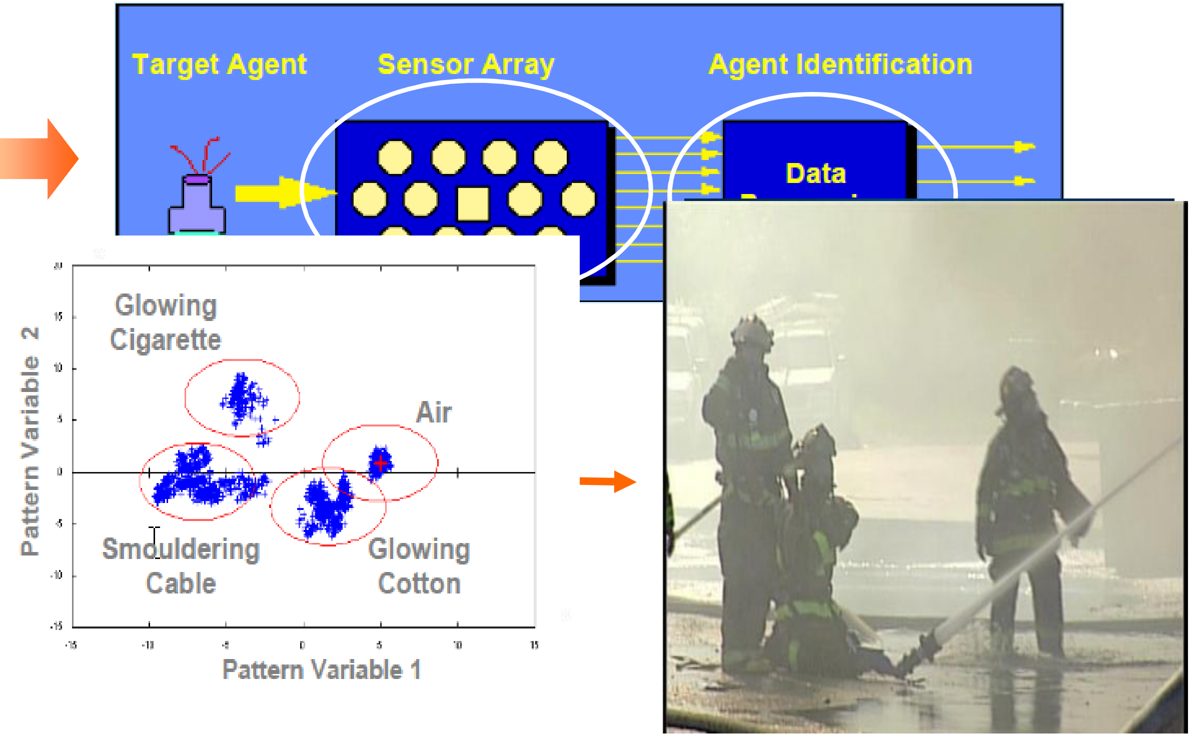
Chemometrics
(Enose)

E-Nose Working Prnciple

Human olfactory system

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



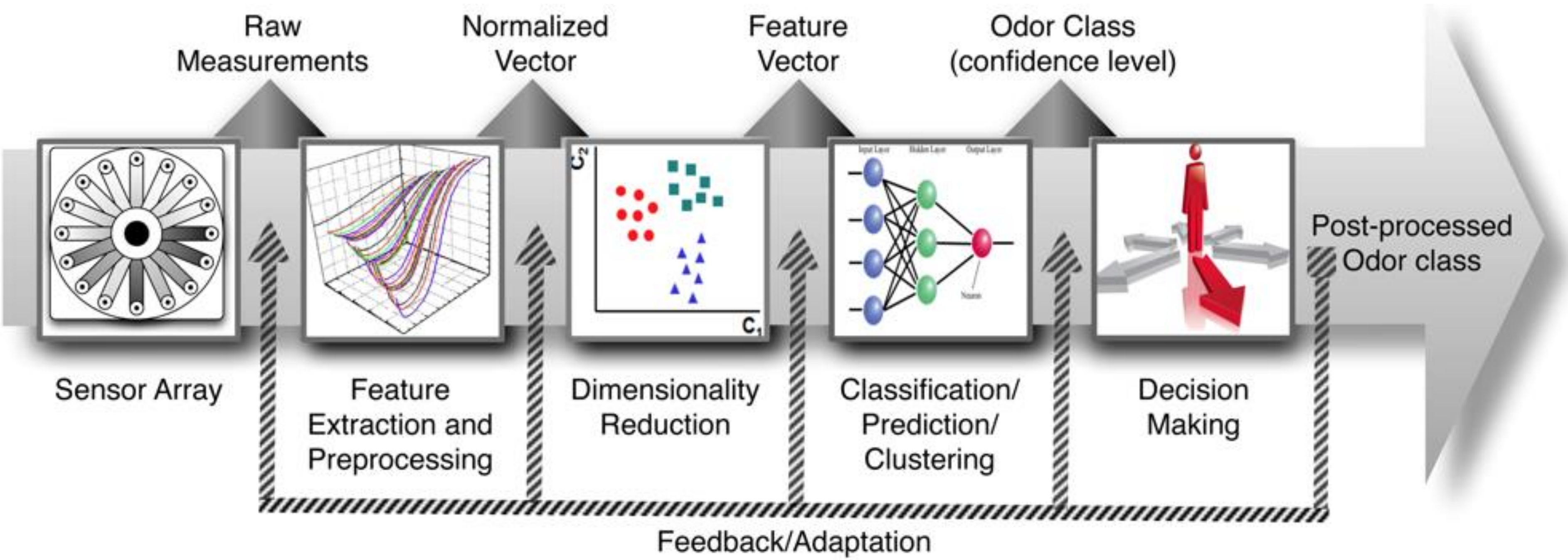


Many Sensors of “Some“ Specificity

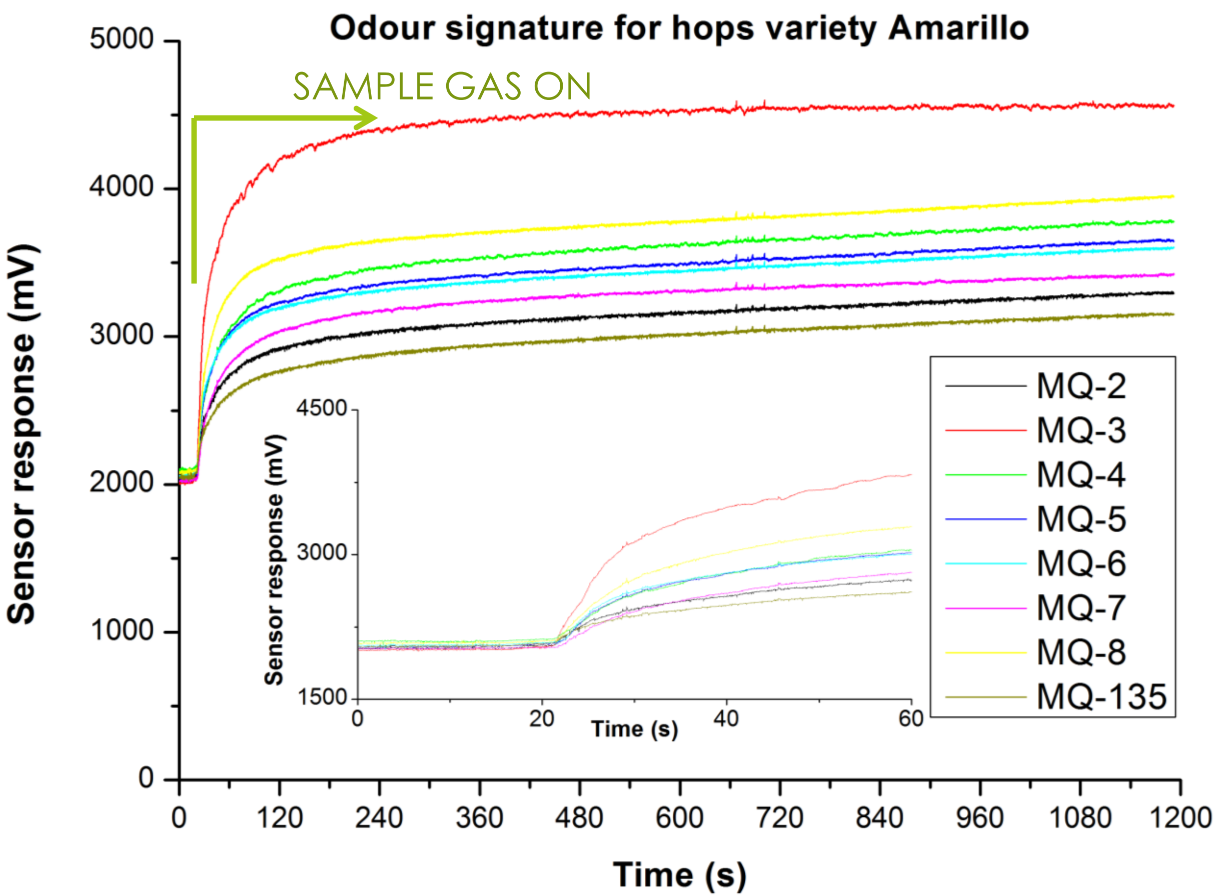
Complex Analyte

Statistical Analysis

E-Nose Detector System



Typical Signals from an Enose Sensor: Beer variaties



Features:

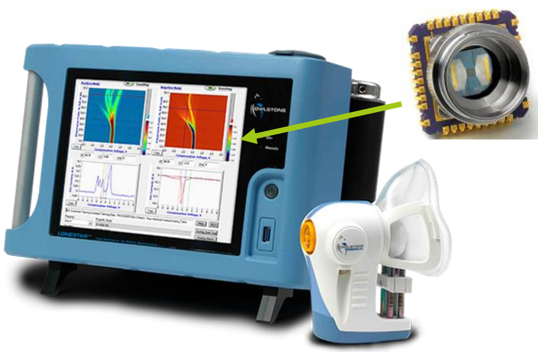
1. Height of response
2. Time constants
   - Multi-exp fits

Challenges @ low conc.

- Sensitivity of fits to drifts
- Selectivity: can we distinguish an analyte in a large gas background

Commercially Available Enose Instruments

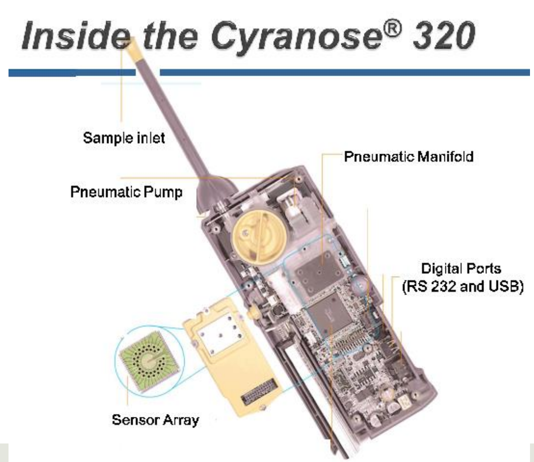
Owlstone Lonestar
(Field Assymetric Ion Mobility)
FAIMS



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

Various Benchtop Chromatography Devices

Airsense
(heated mox sensor array)



Cyranose
(array of NP-doped polymers)

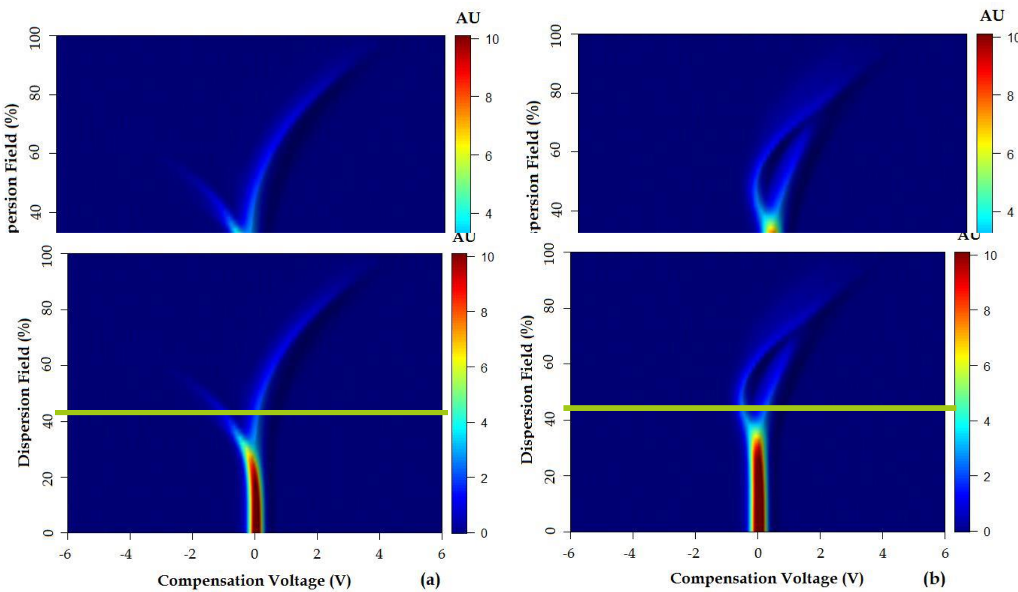
ETC.

Olfactory Detection of Rot

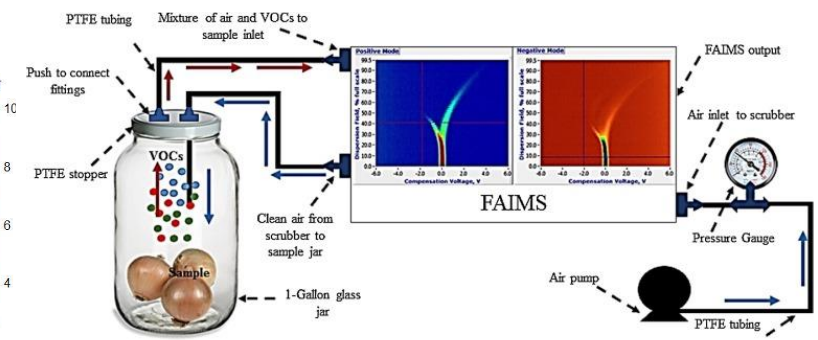
Detection of Potato Storage Disease via Gas Analysis: A Pilot Study Using Field Asymmetric Ion Mobility Spectrometry

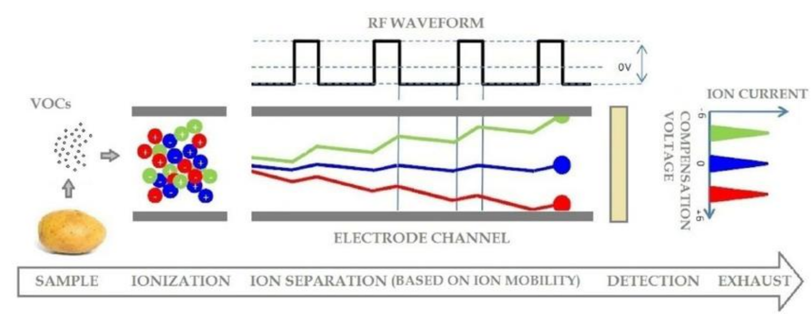
Massimo Rutolo [1,*], James A. Covington [1], John Clarkson [2] and Daciana Iliescu [1]

Sensors **2014**, *14*, 15939-15952; doi:10.3390/s140915939



Gas ions mobility spectra





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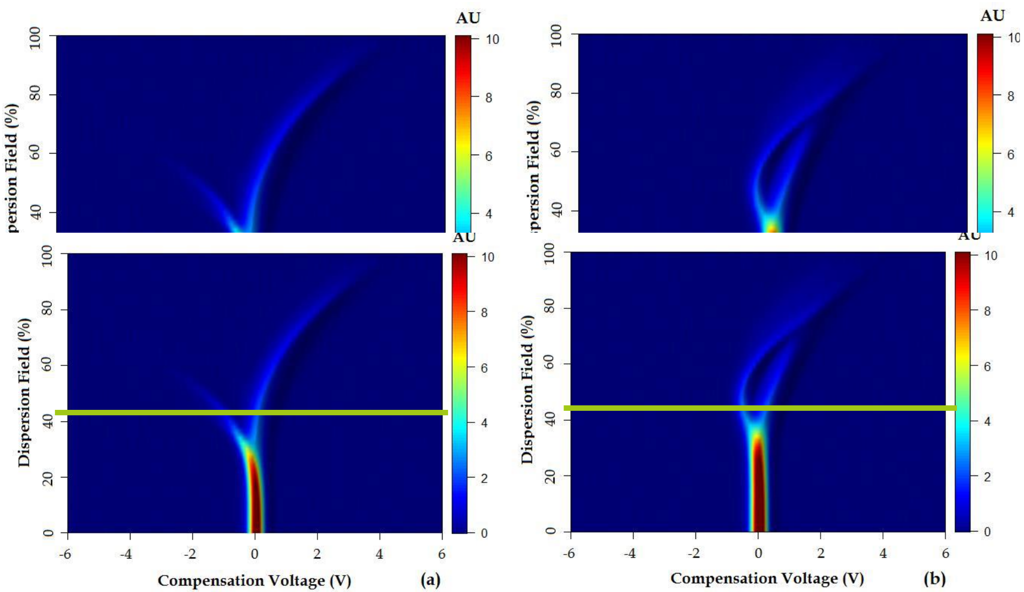

Gas ions mobility spectra

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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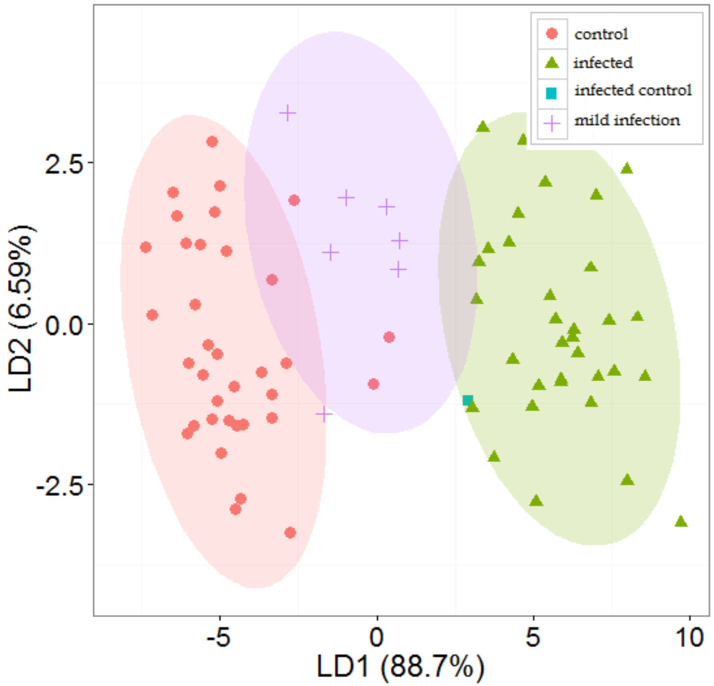

Many Literature Studies dating back to 1990s

Different Types of Rot

Different Biomarkers

VOC Fingerprinting

Olfactory Detection of Rot

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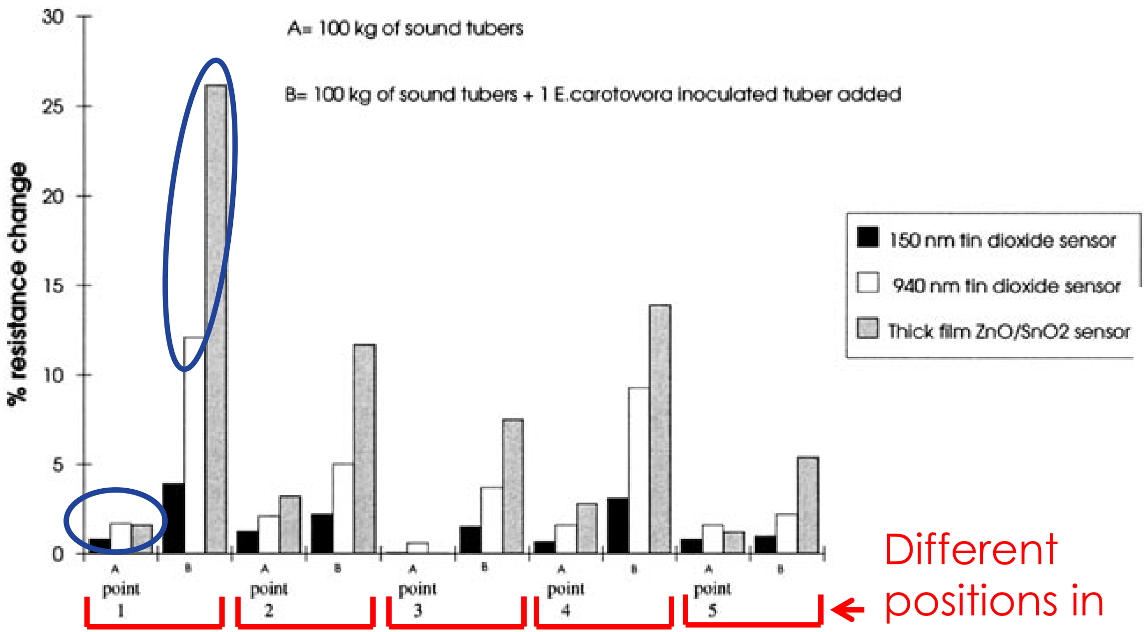
The development of a sensor system for the early detection of soft rot in stored potato tubers

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



Different positions in a crate

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 Montsma

FOOD & BIOBASED RESEARCH WAGENINGEN UR

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

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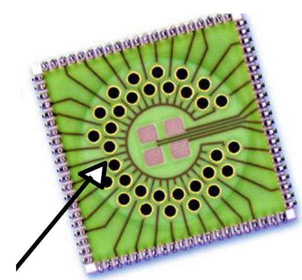
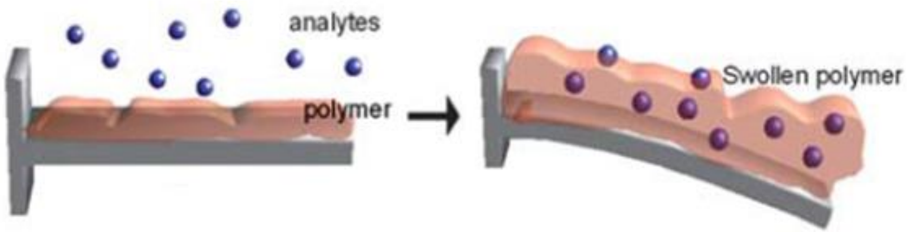
Chip-based Dispersed Disposables

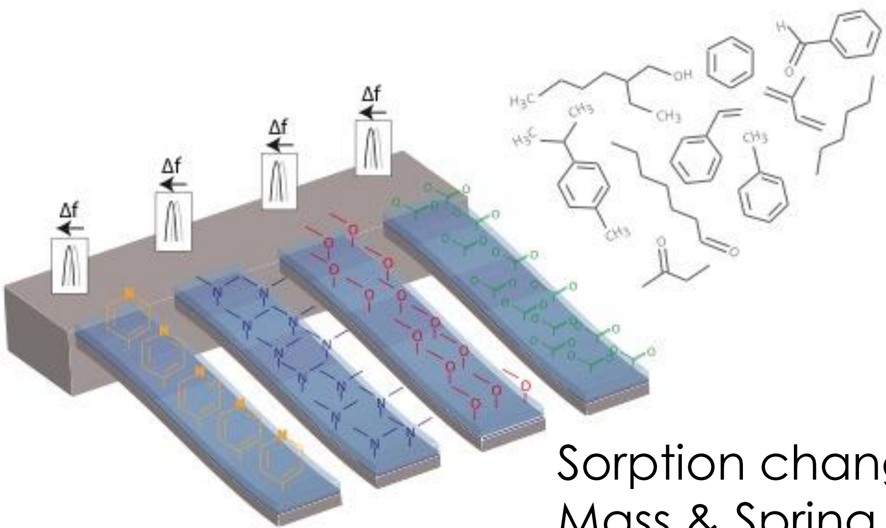
- Distribute sensing chips inside the storage
- Sensors communicate measured data periodically
- Can be salvaged later

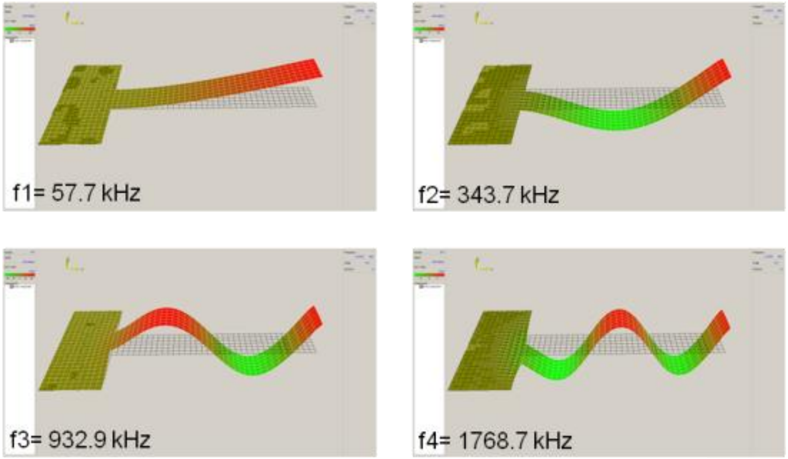


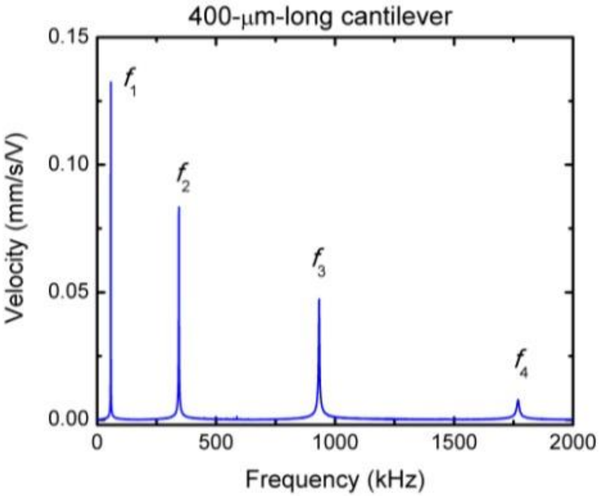
FEASIBILITY?

MicroCantilever Principle

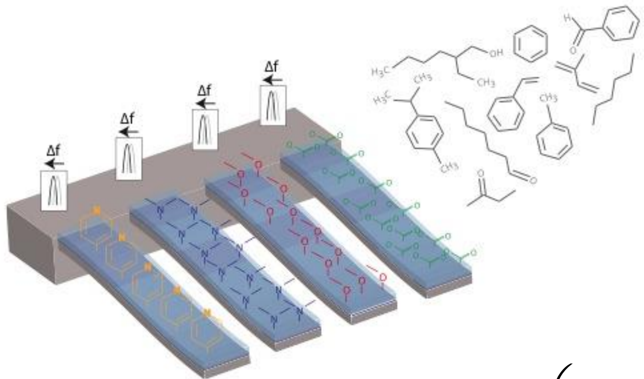




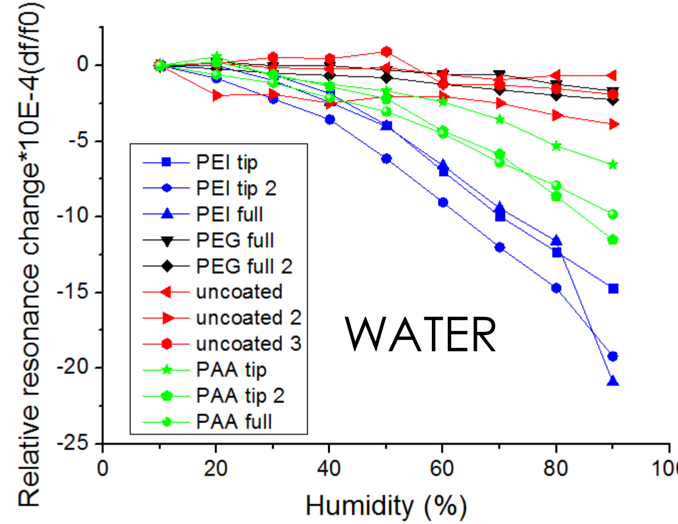


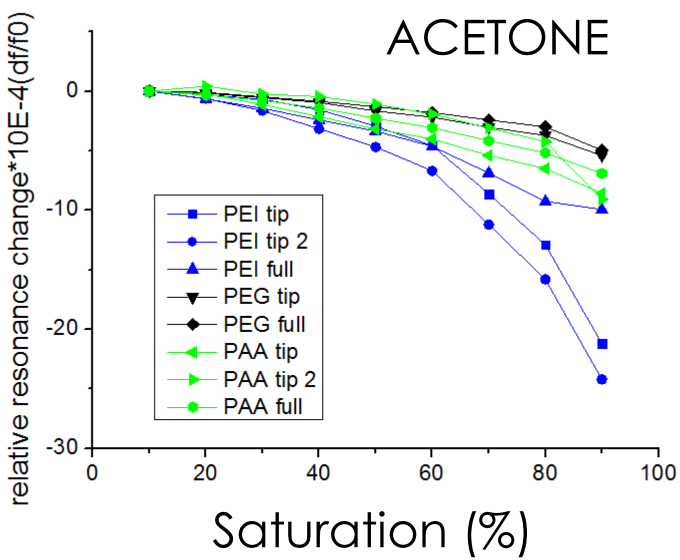


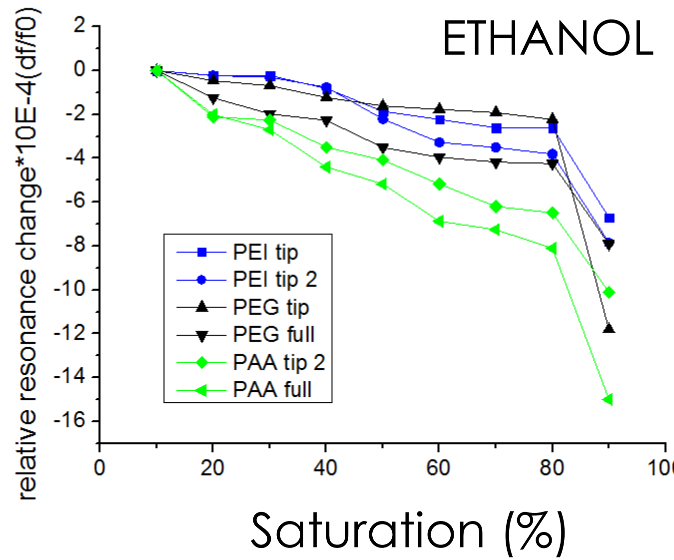
Sorption changes
Mass & Spring constant
➔ Resonant f shift



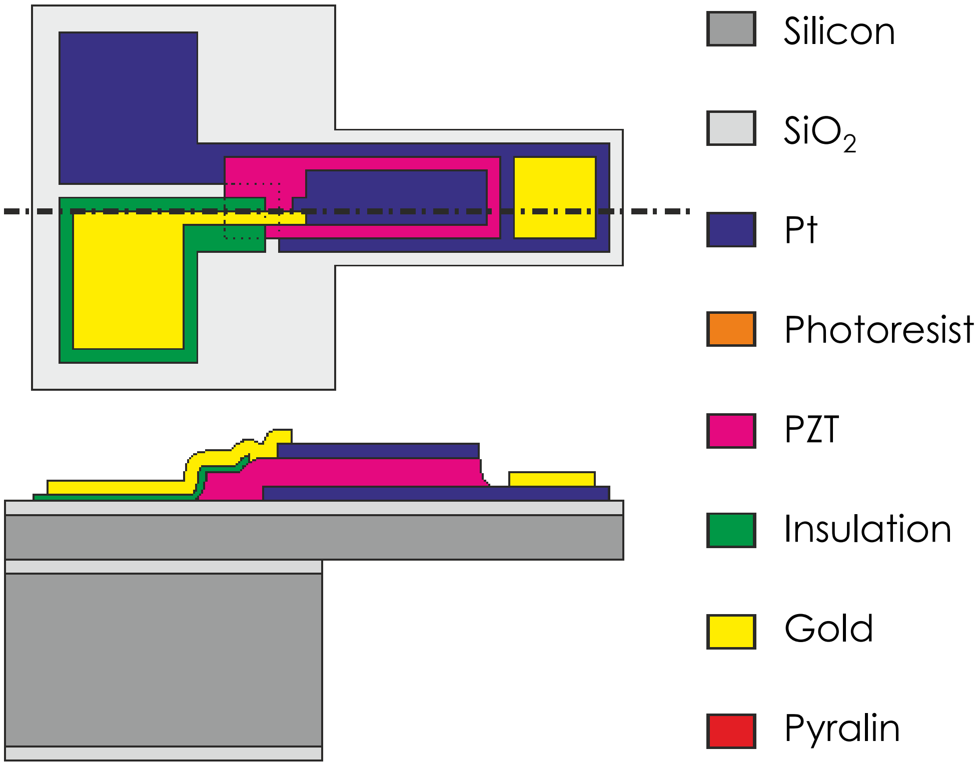
$$\frac{\Delta f}{f} = \frac{1}{2}\left(\frac{\Delta k}{k} - \frac{\Delta m}{m}\right)$$

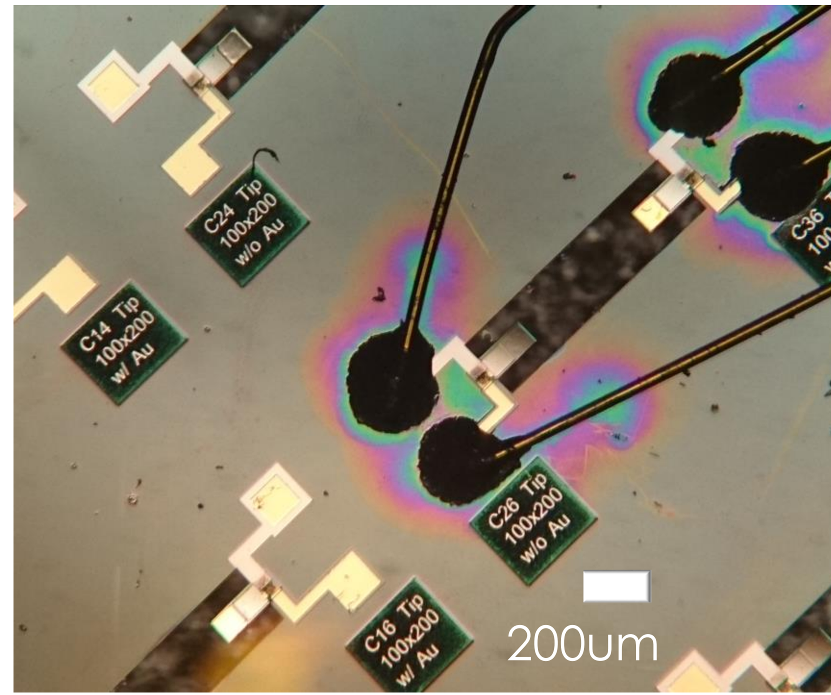






Piezoelectric MEMS cantilever with PZT Layer





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

$$\left(\frac{\Delta m}{S}\right)_{min} \approx h\rho_b \sqrt{\frac{Bk_B T}{\pi^2 A^2 m_b Q f_n{}^3}}$$

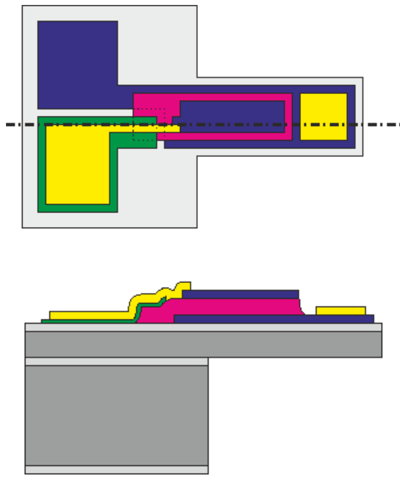
A=Displacement amplitude

Device & Ref	Device area (μm^2)	Resonance Frequency (MHz)	Quality factor	Surface sensitivity ($cm^2.g^{-1}$)	Minimum Relative Frequency deviation	SMLOD ($zg.\mu m^{-2}$)	DMMP Concentration resolution (measured) (ppb)	DMMP Concentration resolution (estimated) (ppb)
FBAR [122]	5×10^4 (b)	1100 (a)	210 (a)	726 (a)	3.6×10^{-7} (b)	10000 (b)	(c)	60 (e)
SAW [34]	5×10^7 (b)	158 (a)	(c)	100 (a)	7×10^{-8} (a)	7000 (b)	87 (b)	42 (a)
CMR [123]	6×10^3 (b)	180 (a)	5×10^4 (a)	2.3×10^3 (b)	1.3×10^{-8} (a)	60 (a)	700 (d)	0.35 (e)
CMUT [124]	1×10^6 (b)	47.7 (a)	140 (a)	4.1×10^3 (b)	1.15×10^{-8} (a)	80.5 (a)	15 (d)	3 (e)
Nano-cantilevers [50]	1.5 (a)	10 (a)	200 (a)	3.75×10^3 (b)	1.5×10^7 (a)	400 (b)	(c)	80 (e)
μ-cantilevers [125][126]	3.2×10^3 (b)	0.1 (a)	80 (a)	2.8×10^3 (b)	10^{-8} (a)	53 (a)	25 (d)	2 (e)

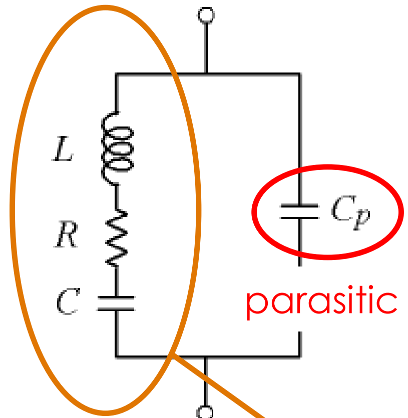
Paul Ivaldi. Modeling, fabrication and characterization of resonant piezoelectric nano mechanical systems for high resolution chemical sensors. Micro and nanotechnologies/Microelectronics. Université de Grenoble, 2014. English. <NNT : 2014GRENT109>. <tel-01192918>

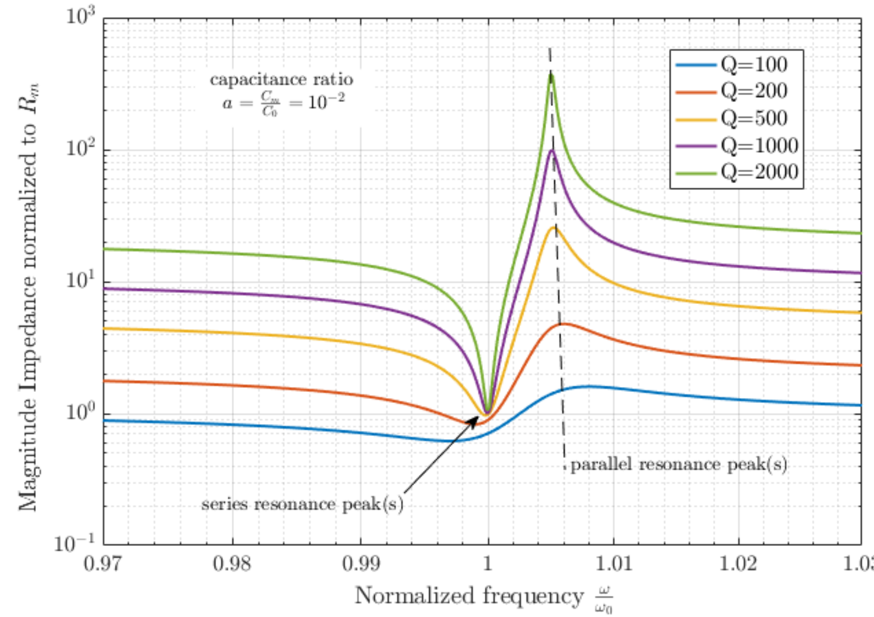
PZT offers high transduction factors
⇒ Higher electronic amplitudes
⇒ Less electronic noise in practice

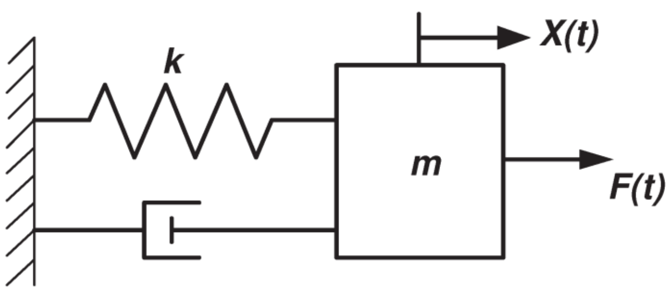
Electronic Readout



Mechanical resonance
Transduced by PZT

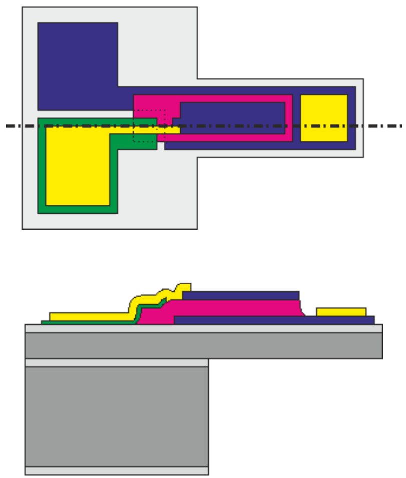




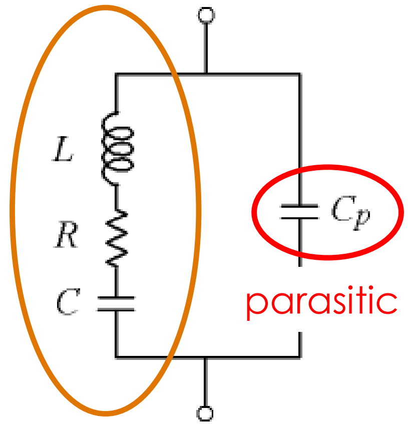


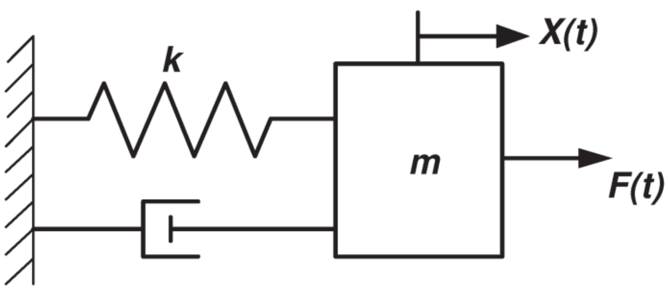
Series peak resonance
influenced by “motional”
parts

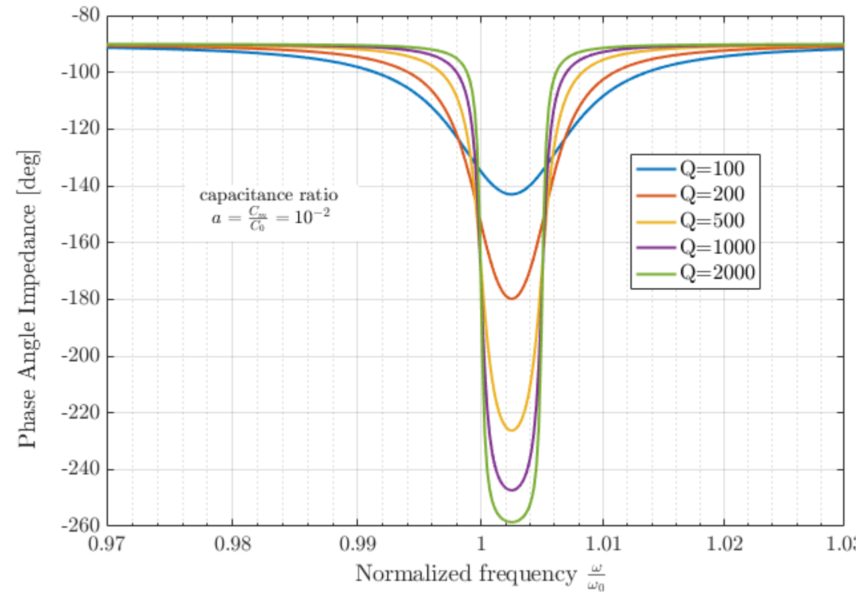
Electronic Readout



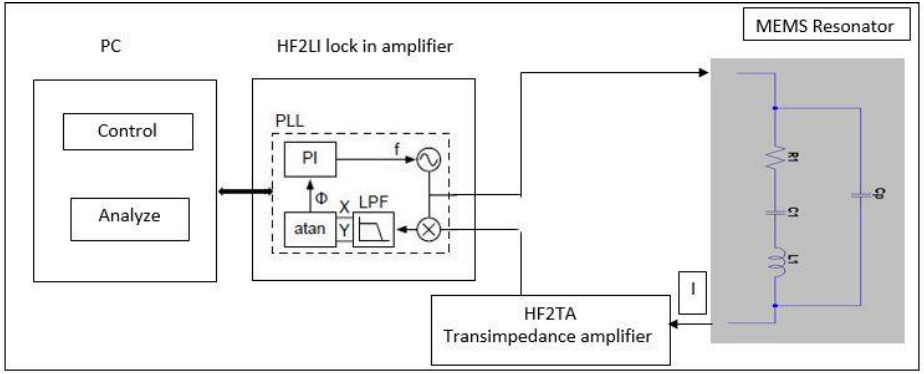
Mechanical resonance
Transduced by PZT

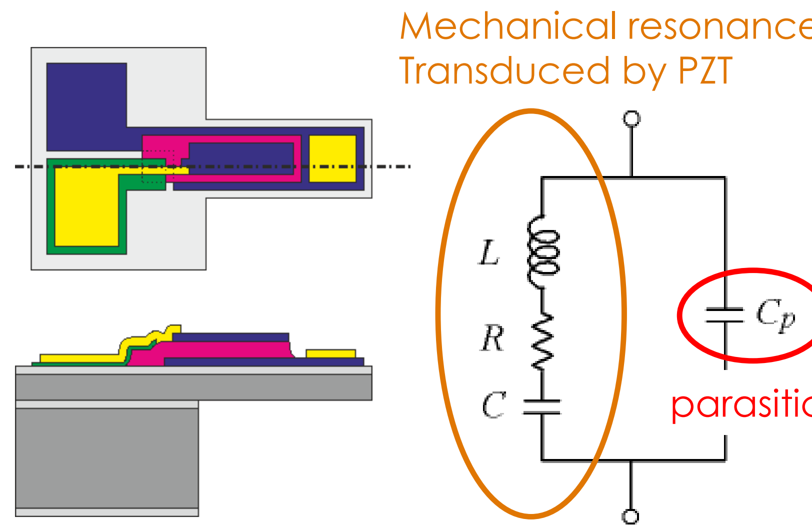


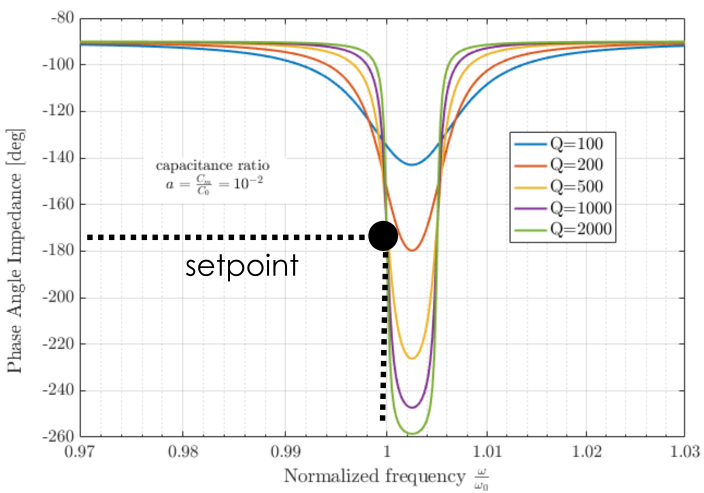




Readout and Measurements: Phase-Locked Loop (PLL)



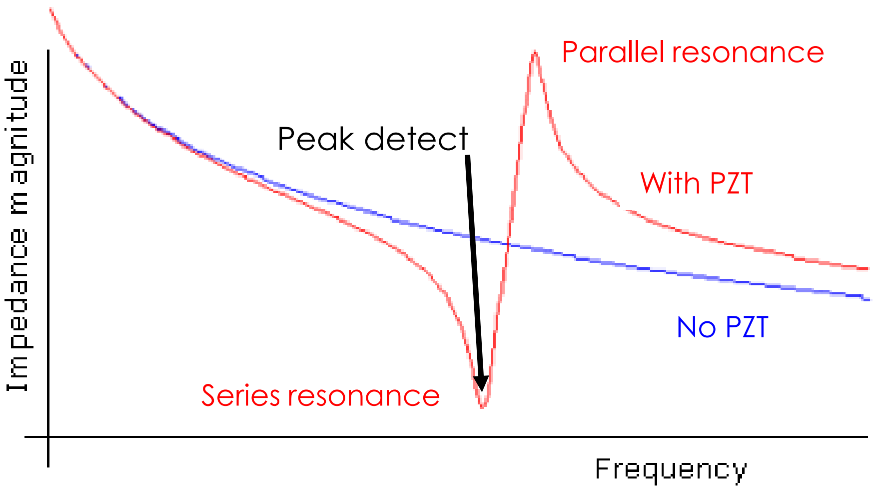




Phase-Lock-Loop Resonator Interface

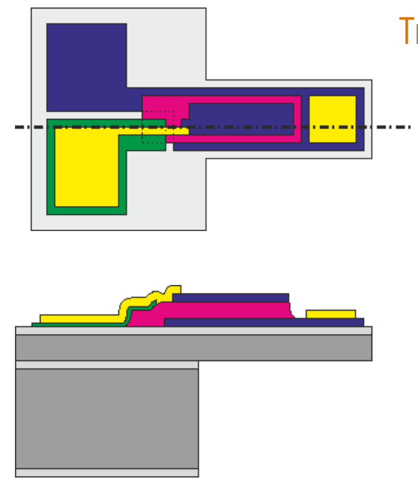
- \+ Tracks resonant *f* automatically
- \+ mHz noise with these sensors
- \- Complex to implement in product
- \- Suffers from C_P variation

Readout and Measurements: Impedance Peak Detection

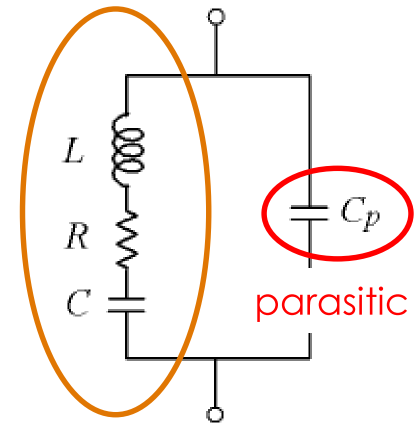


Impedance Peak Resonator Interface

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



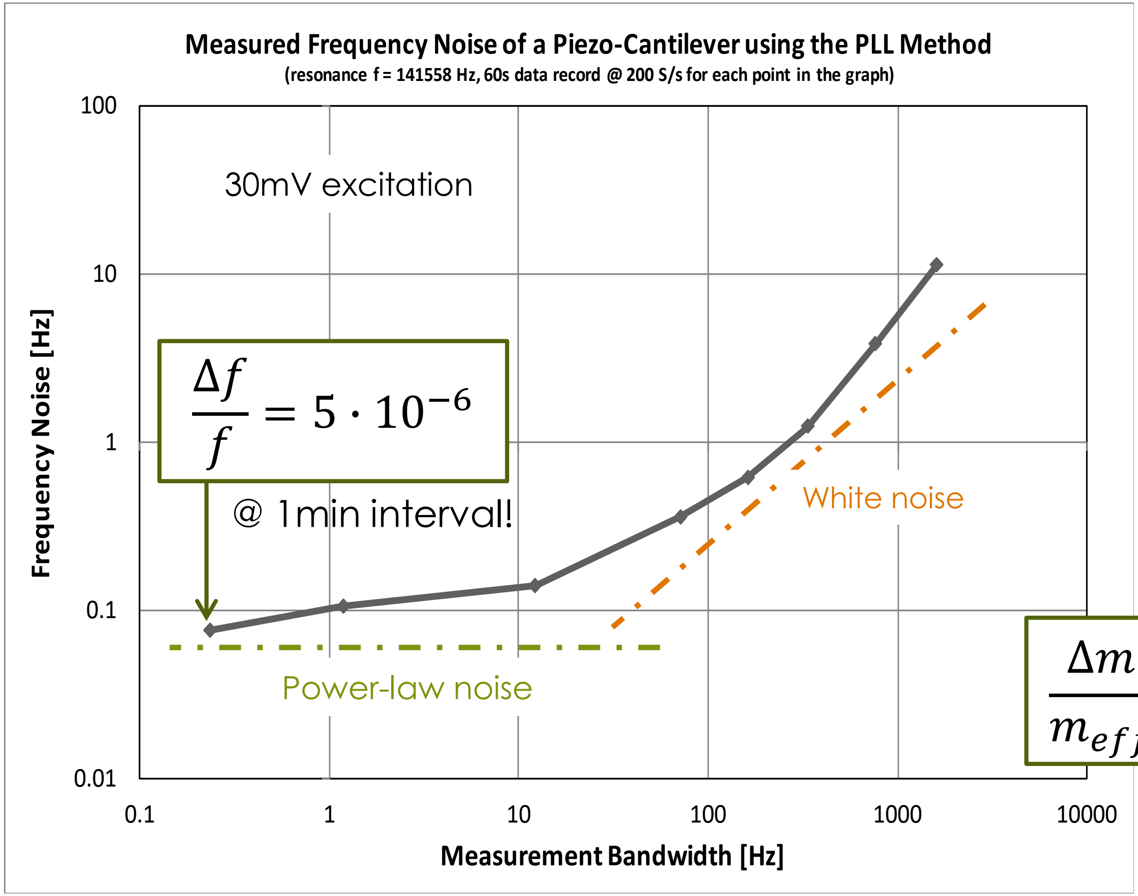
Mechanical resonance Transduced by PZT



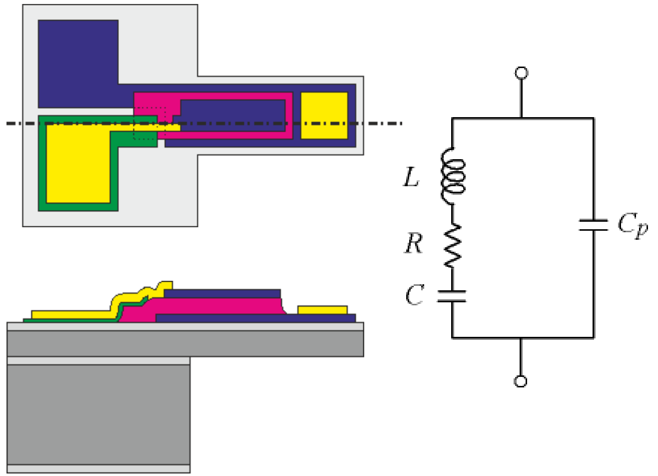
$$f_{series} = \frac{1}{2p\sqrt{LC}} \text{ o } \sqrt{\frac{k}{m}}$$ ✓

$$f_{paralel} = \frac{1}{2p\sqrt{L\left(C \,\|\, C_P\right)}}$$ ✗

Readout and Measurements



$$\frac{\Delta f}{f} = 5 \cdot 10^{-6}$$



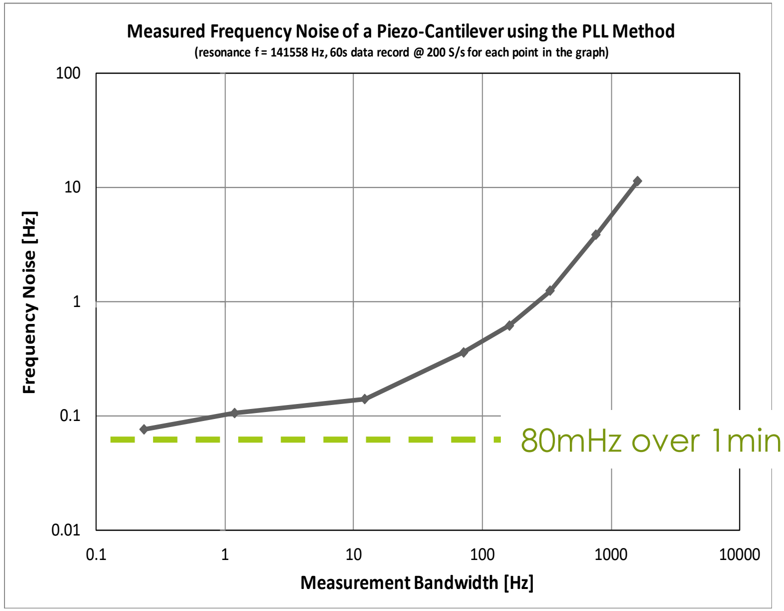
$$\frac{\Delta m}{m_{eff}} = 2\frac{\Delta f}{f} \Rightarrow \left(\frac{\Delta m}{S}\right)_{min} \cong 100\,\frac{\mathrm{ag}}{\mu\mathrm{m}^2}$$

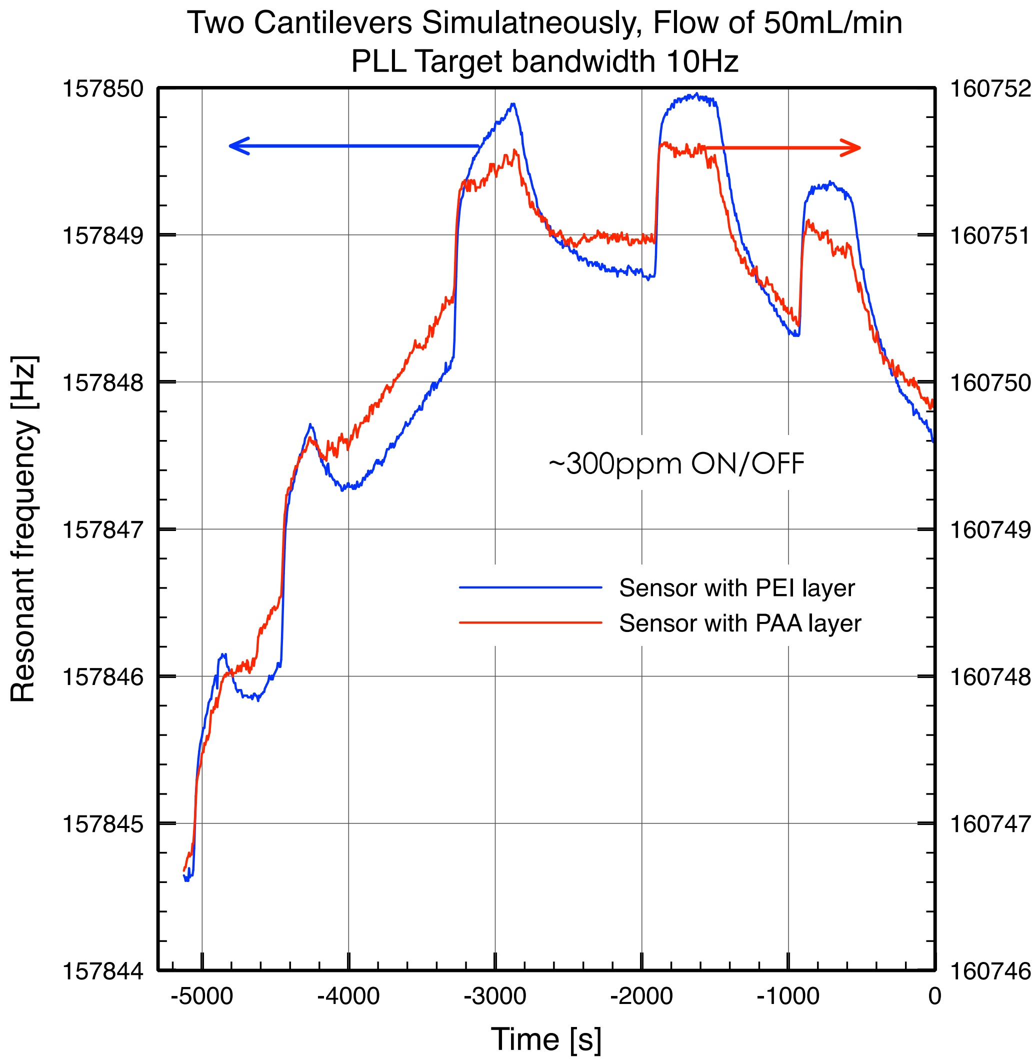
Practical SMLOD
(on a 1min data record)

Measurements: ACETONE in N_2

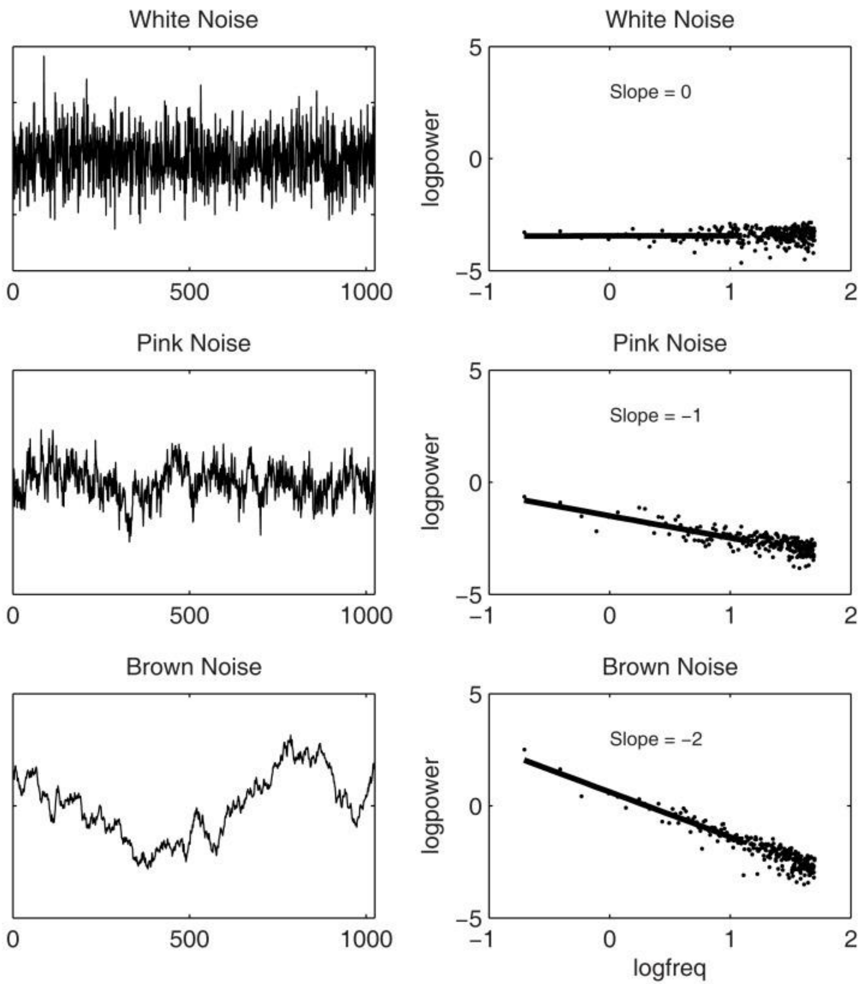
$$S_{PEI} = 4\,\frac{\text{mHz}}{\text{ppm}} \qquad S_{PAA} = 2\,\frac{\text{mHz}}{\text{ppm}}$$

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

THERMO-MECHANICAL NOISE

- White Power Spectrum
- Due to Intrinsic Acoustic Losses
- Due to Air Friction

ELECTRONIC NOISE

- White Power Spectrum
- + $1/f$ + $1/f^2$ + … Power Spectrum
- Due to Intrinsic Electronic Losses

THERMAL FLUCTIATION NOISE

- White Power Spectrum
- Due to Sensitivity of ω_0 on T

DIFFUSION AND ABSORPTION/DESORPTION NOISE

- Complex Power Spectrum
- Due to Ab/De-sorption & Diffusion of Species Along the Surface

Resonant Sensor Noise Sources

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THERMO-MECHANICAL NOISE

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LIMITS IN PRACTICE!

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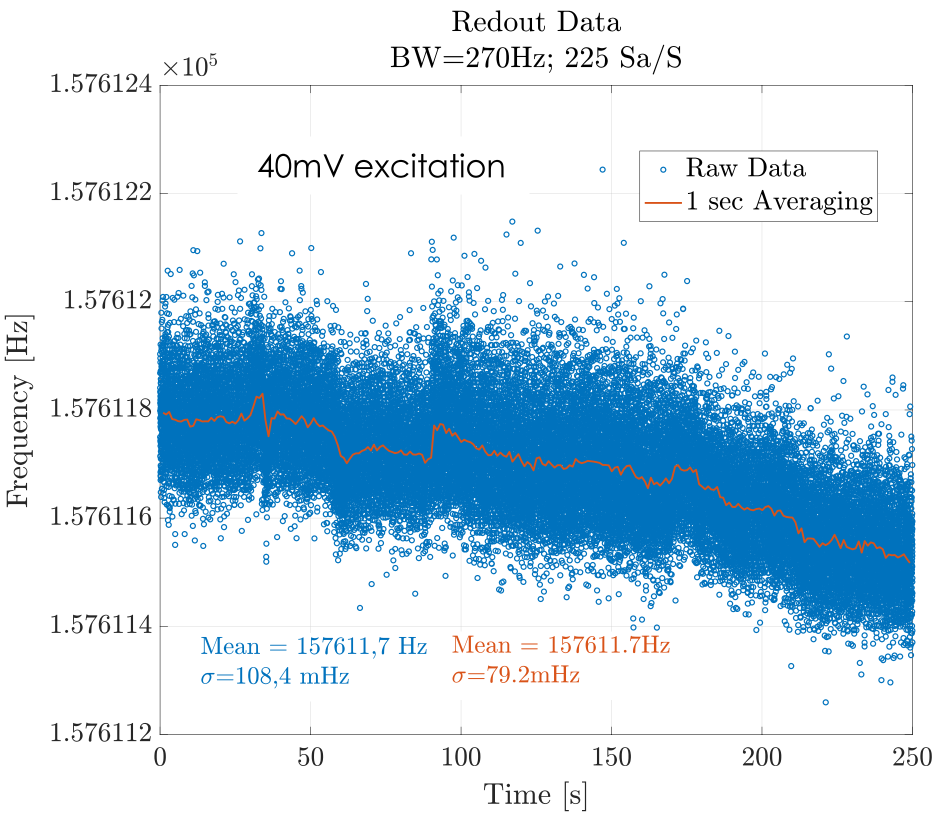
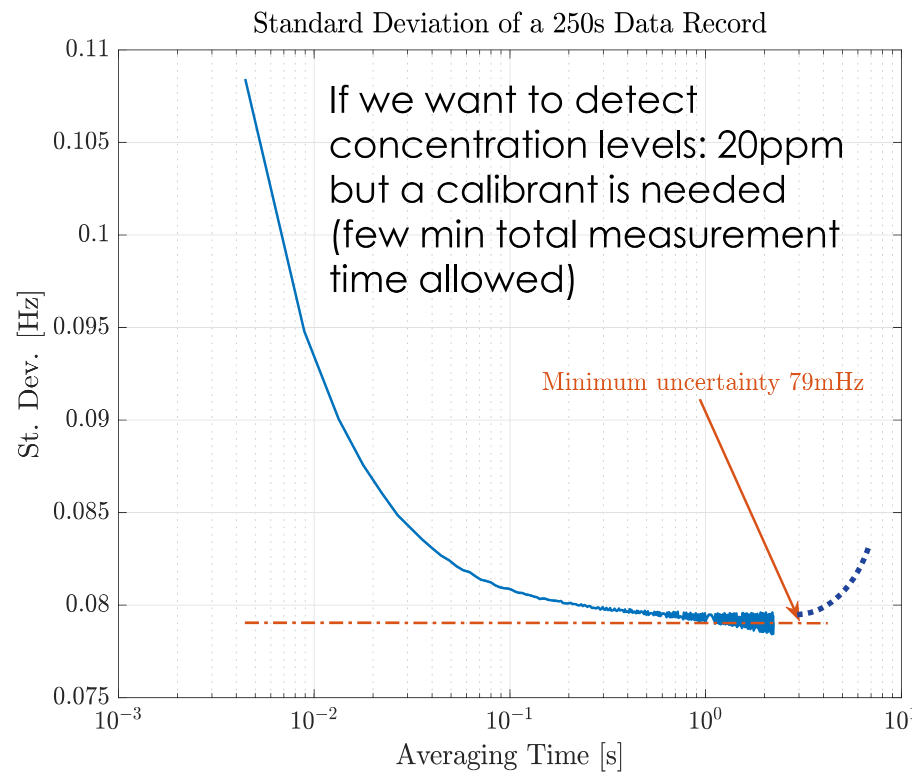
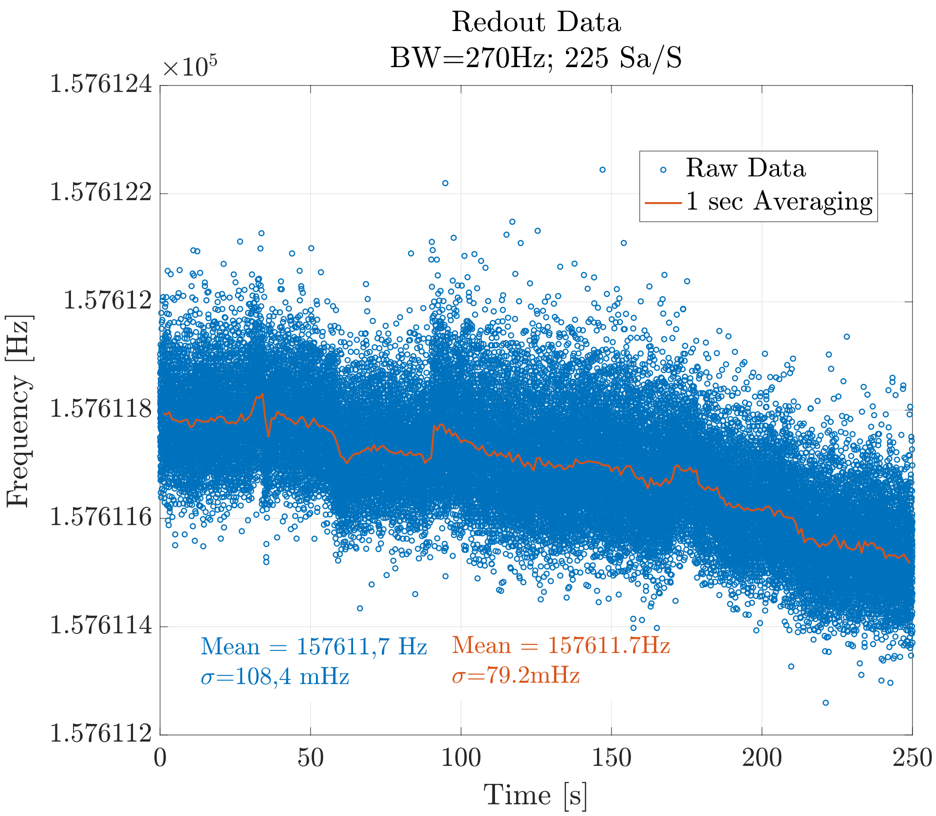
Resonator Noise Analysis: Allan Deviation



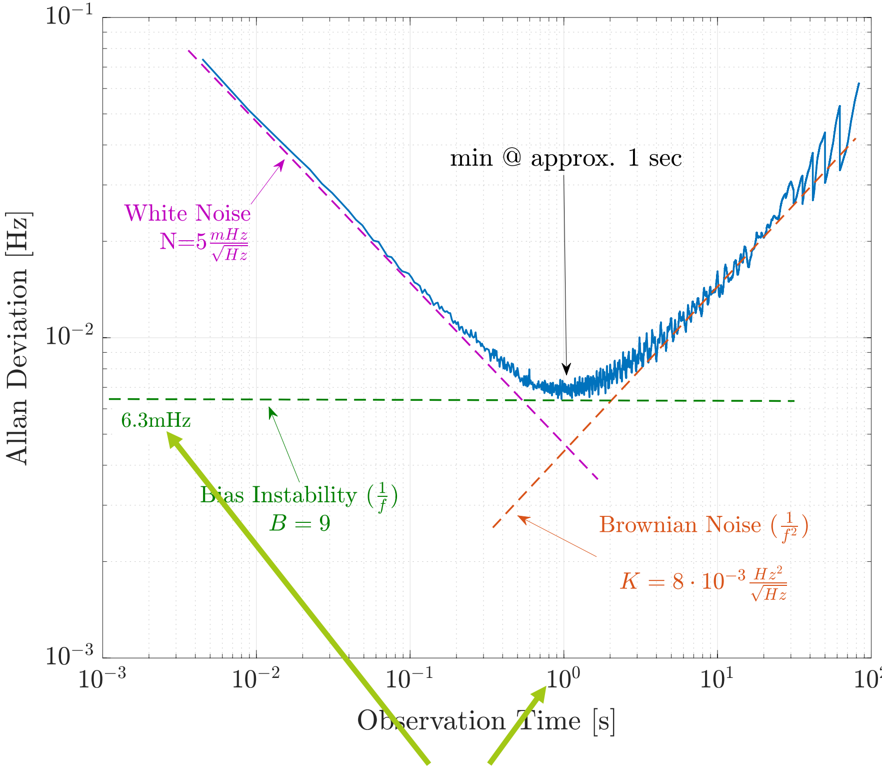


If we want to detect concentration levels: 20ppm but a calibrant is needed (few min total measurement time allowed)

Resonator Noise Analysis: Allan Deviation

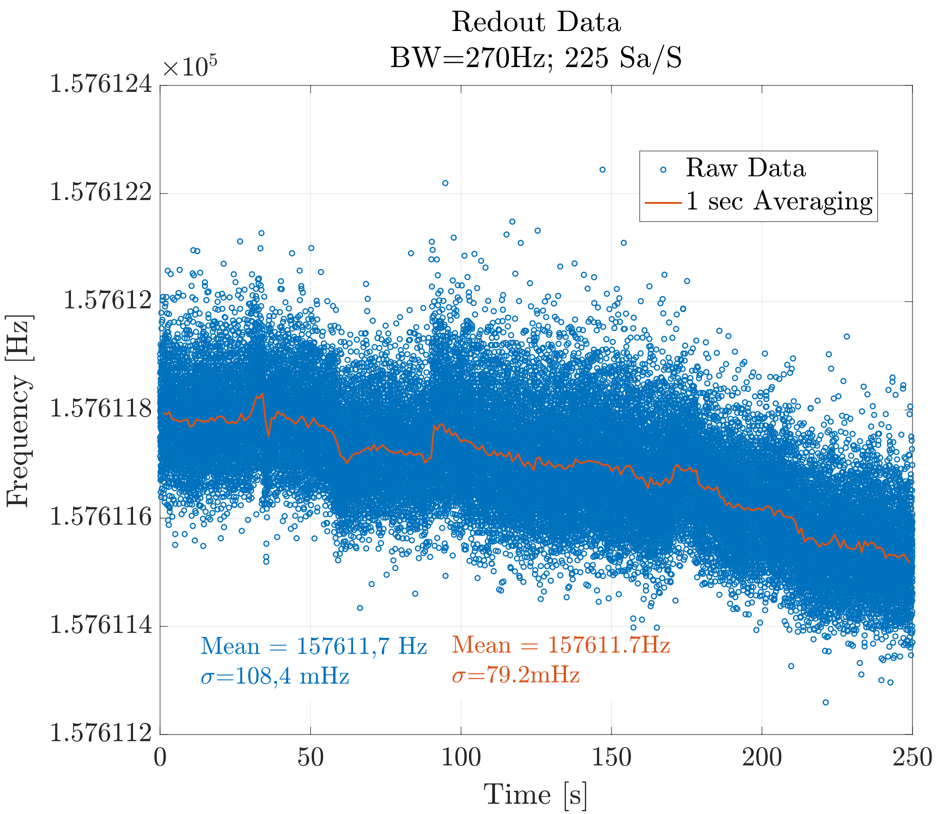


EXPECTED INNACURACY BETWEEN NEIGHBOURING MEASUREMENTS

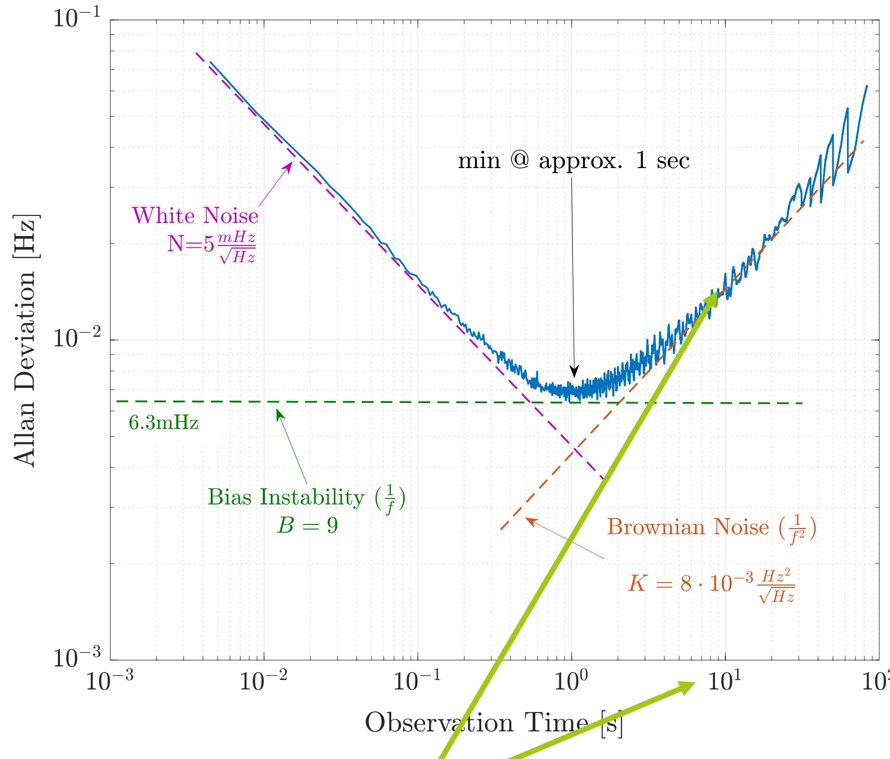


If we want to detect concentration rate changes: 1.5ppm/sec

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

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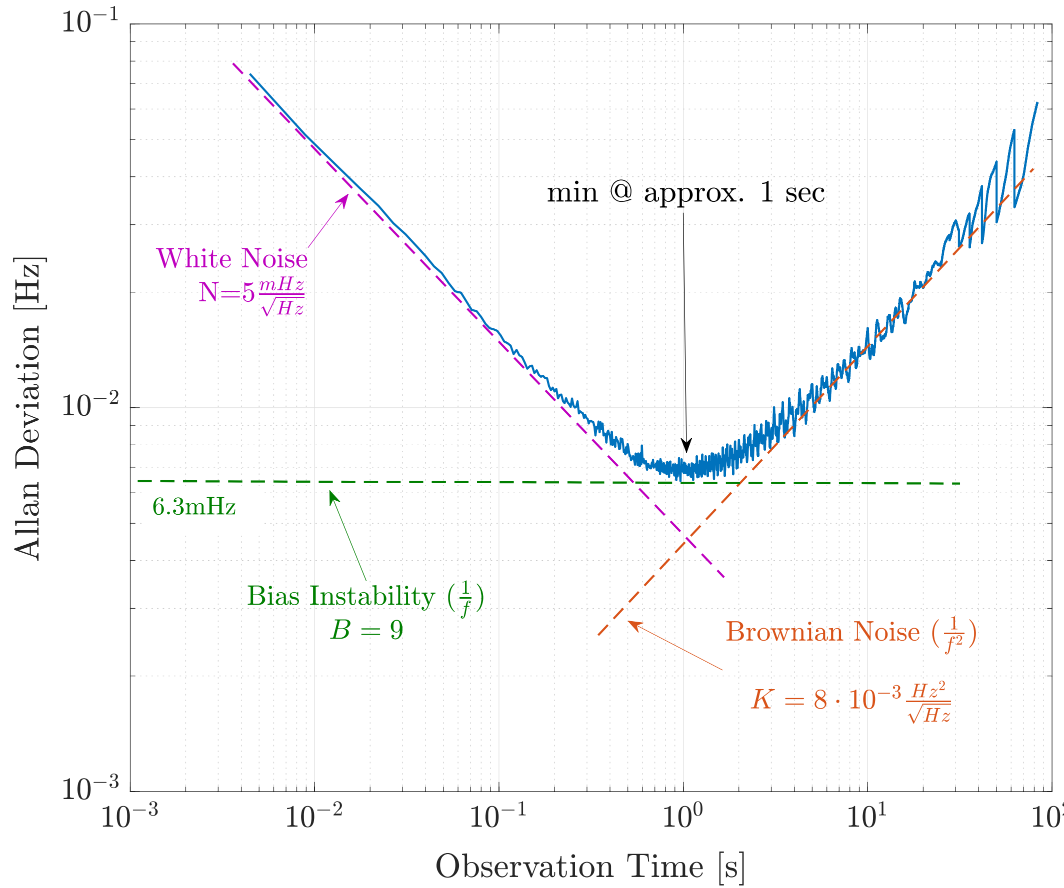
Detecting Rot in Potatoes:

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 Reccomendations

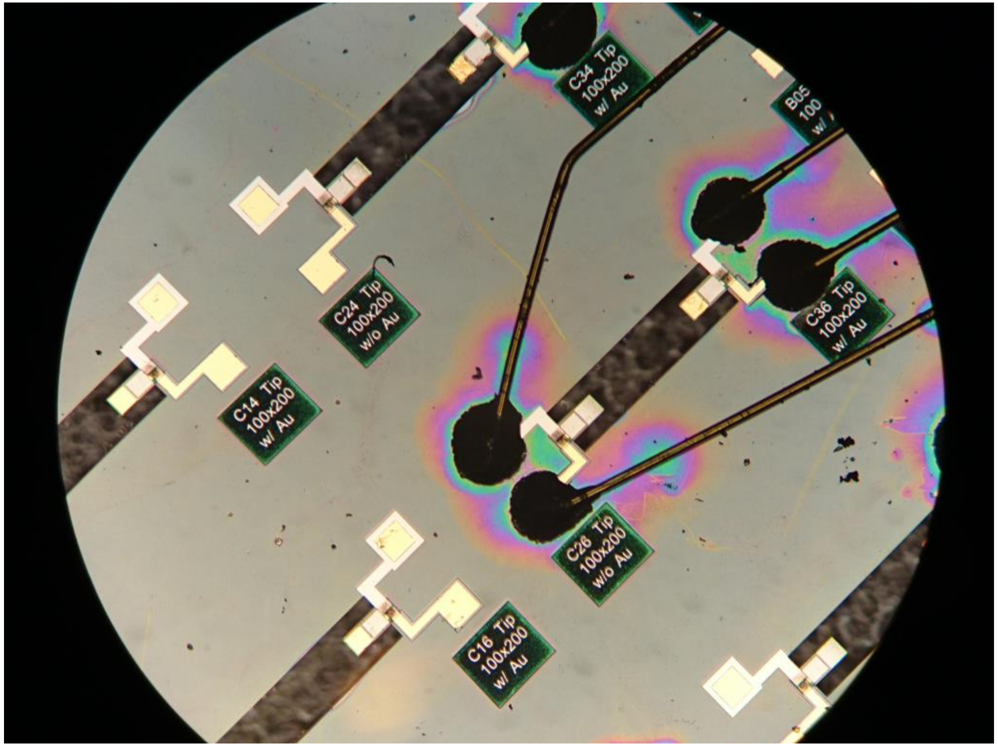
Detection of potato rot via E-nose is present in literature and prior work.

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 $1/f^2$ (brown) noise by more than 10 times
- Improving Q-factor is not a priority; find ways to increase max. amplitude instead



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Albert van Hoorn

and all students that contributed greatly.

Tolsma Storage Technology

Grisnich

Members of the Tolsma-Grisnich Group

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Questions?

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