Inkjetted arrays of gold-nanocluster chemiresistors for end-of-service-life indicators in respiratory cartridges. Electrode scaling effects.

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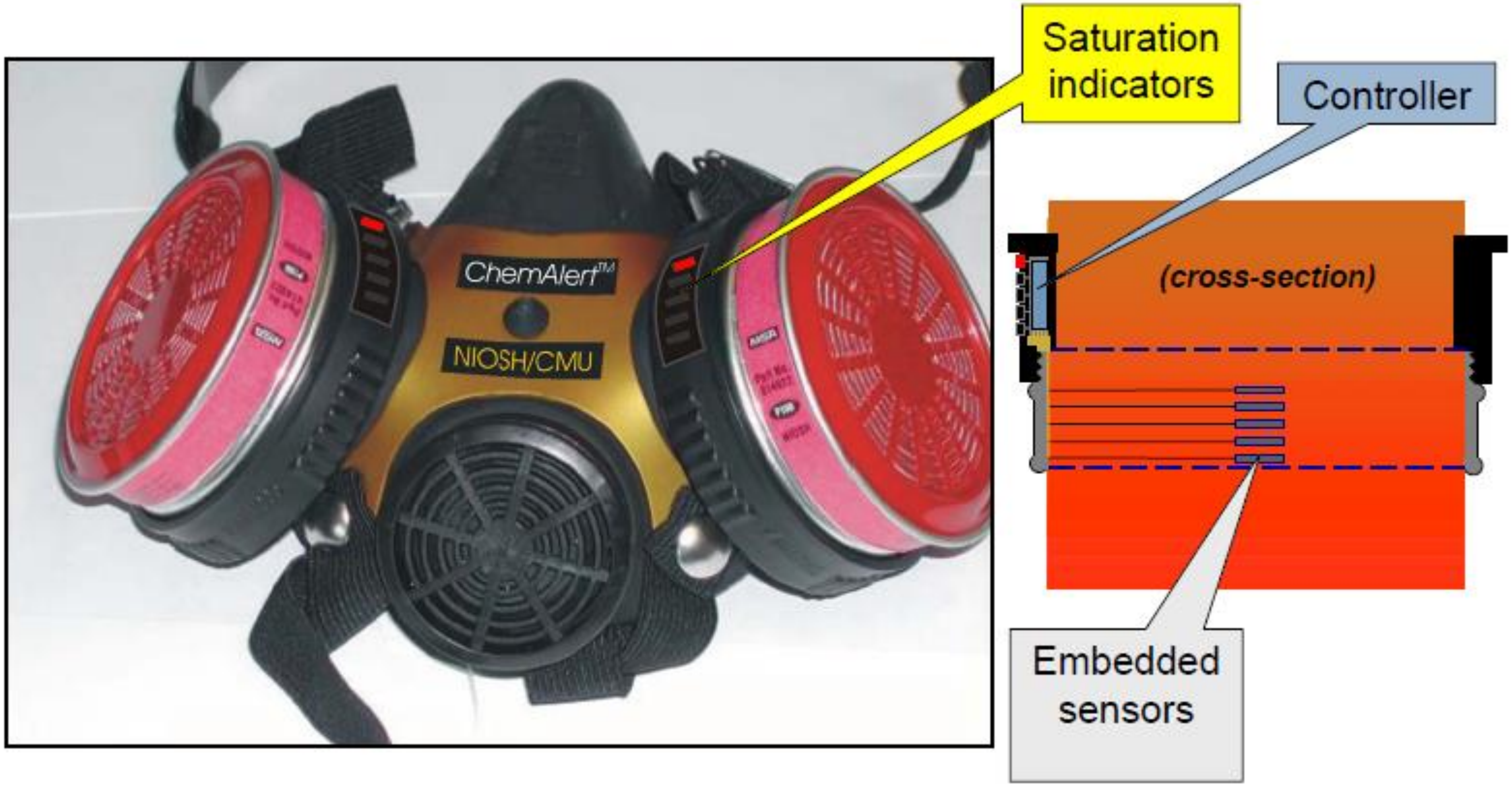
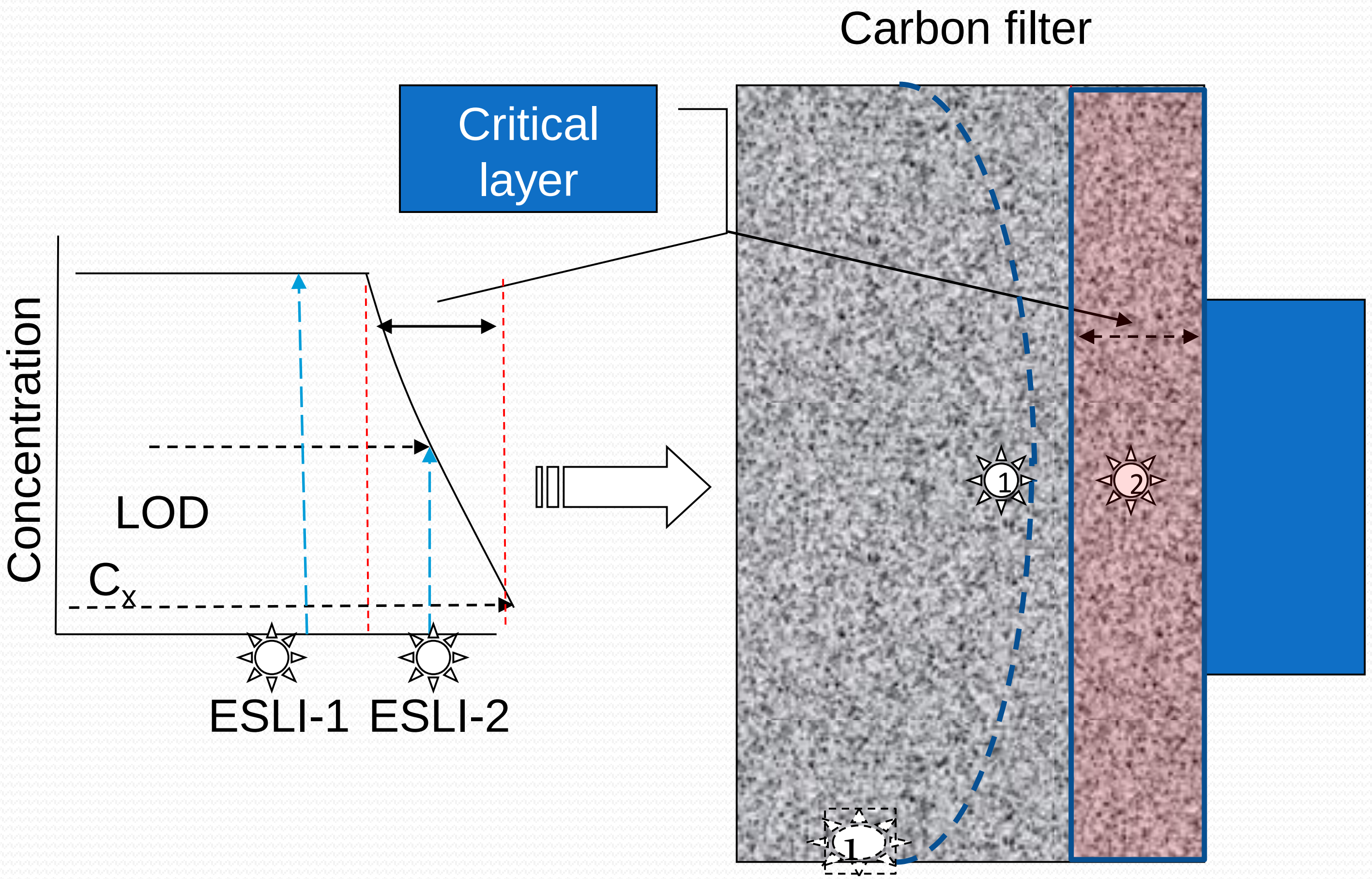
Gary K. Fedder, CMU, USA



In 1998, OSHA recommended that all respirators be equipped with a NIOSH certified End of Service Life Indicator (ESLI) for the expected contaminant or,
if no ESLI exists, implement a cartridge change schedule to replace the cartridge prior to breakthrough



- **small**
- **sensitive**
- **discriminate** between **humidity** and analytes.
- **insensitive to temperature** changes.
- **robust** and **inexpensive**.

A color changing indicator is a desired solution,

A second best will be a temperature-compensated miniature array of passive chemical sensors.

Miniature chemiresistive array for ESLI

- Monolayer protected gold nanoclusters : sensitivity, selectivity, variety, solubility.
- Inkjetting, preferred technology for deposition of different sensitive materials on a small space. Thickness control by multiple jetting/drying cycles.
- Due to high intrinsic resistivity of the material, interdigitated electrode transducers (IDT) are required.
- “Spiral” (circular) intertwined transducers for best material economy and spatial control.

Monolayer protected metal nanoclusters (MPC) or (MPN).

Brust and Shiffrin first synthesis 1994.

Wohltjen and Snow Chem. Mater., and Anal. Chem. 1998.

Composite materials consisting of a cluster of gold atoms surrounded by a single layer of an organic molecule bound to the metal through a sulfur atom.

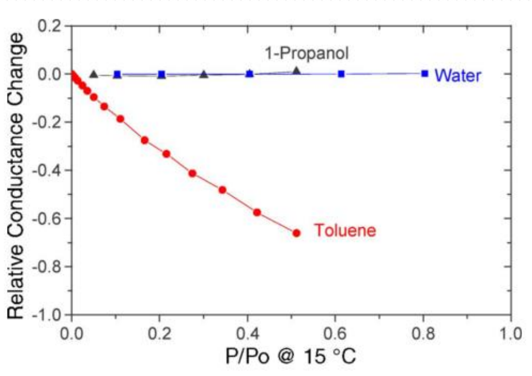
•Naturally occurring and well defined sub-percolation state.

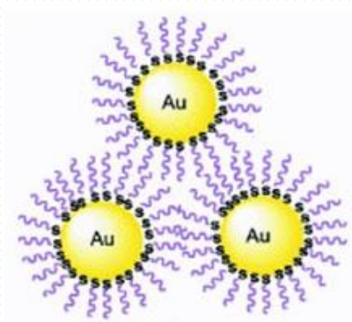
•Proximity between conducting islands is controlled by monolayer size.

•Response: Swelling and dielectric constant changes induced by absorption.

•Solubility, sensitivity and selectivity can be controlled by synthesis.

•Fast response time.





1-2 nm core, 0.6 nm shell

Phenyl-C_2H_4SH

$\underline{C_8H_{17}SH}$

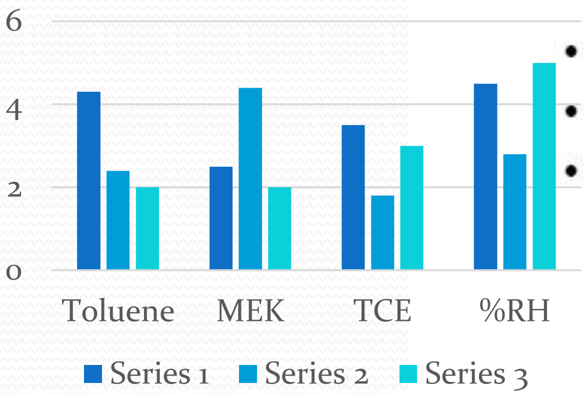
$C_6H_{13}SH$

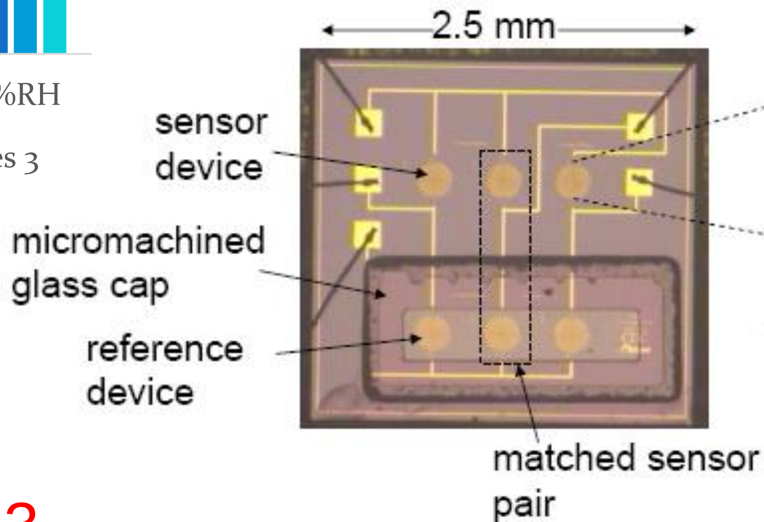
OH-$C_6H_{12}SH$

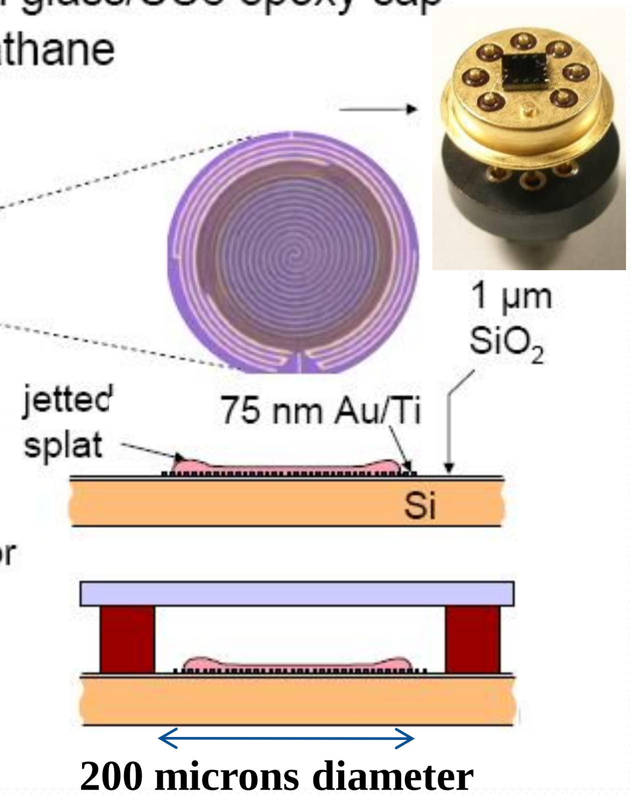
HOOC-$C_{11}H_{22}SH$

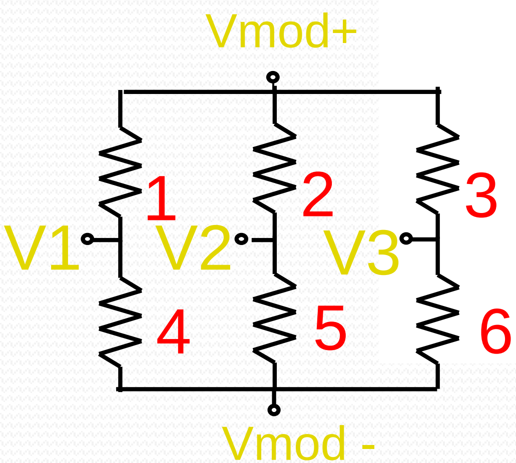
Sensor Circuit Chip

- 3 chemiresistive sensor circuits
- Reference devices capped with glass/SU8 epoxy cap
- Sealed with low outgassing arathane





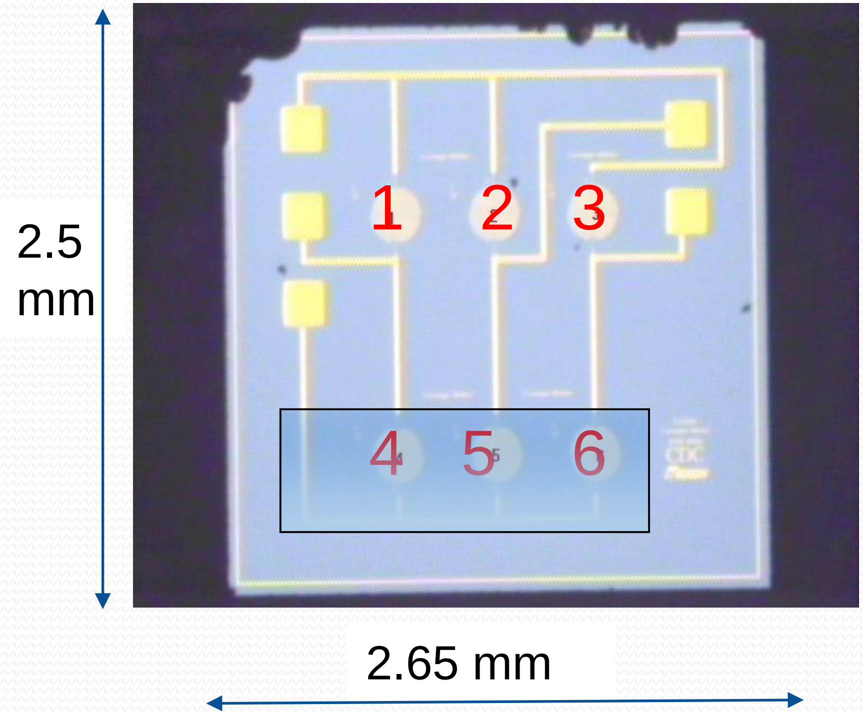


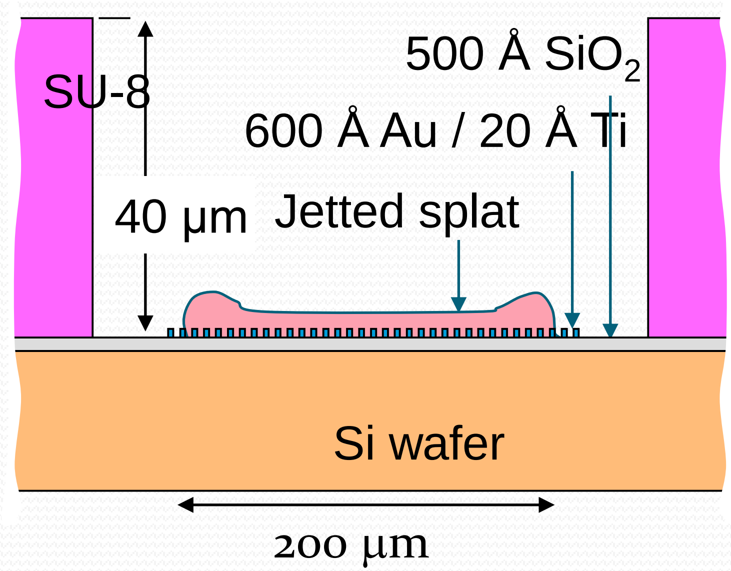


$$\Delta V_1 = V_s \frac{\Delta R}{R_0 + R_1}$$

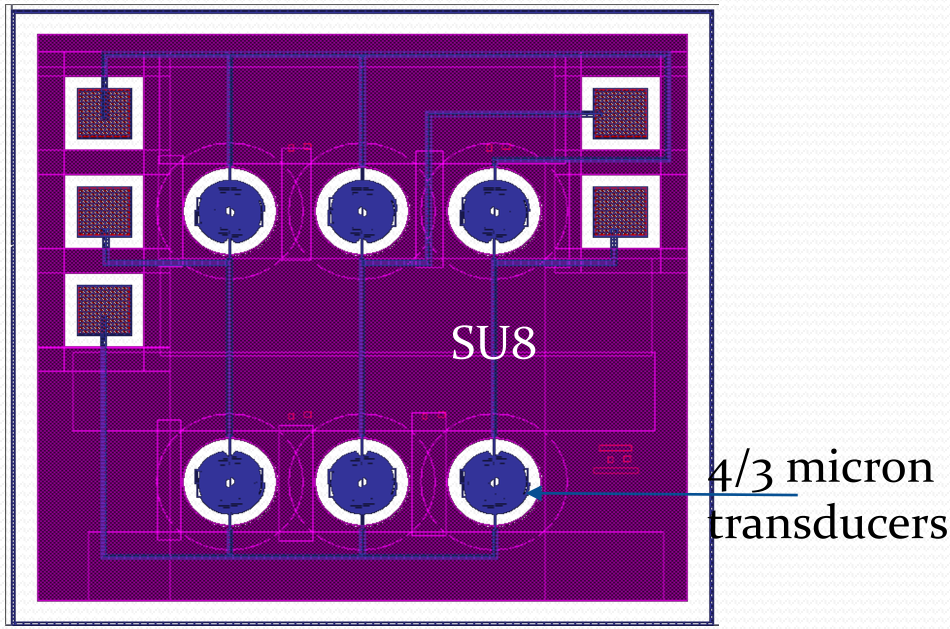
Fedder, G.K. et al. *12th International meeting on Chemical Sensors (ICMS12)*, July 13-16, 2008, Columbus, Ohio.

Gen III

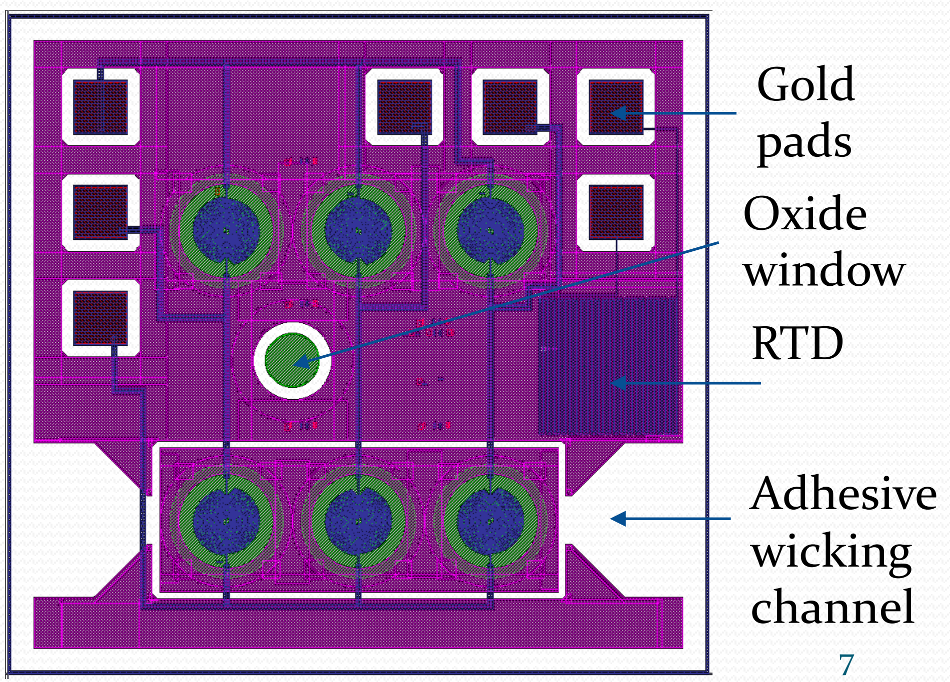




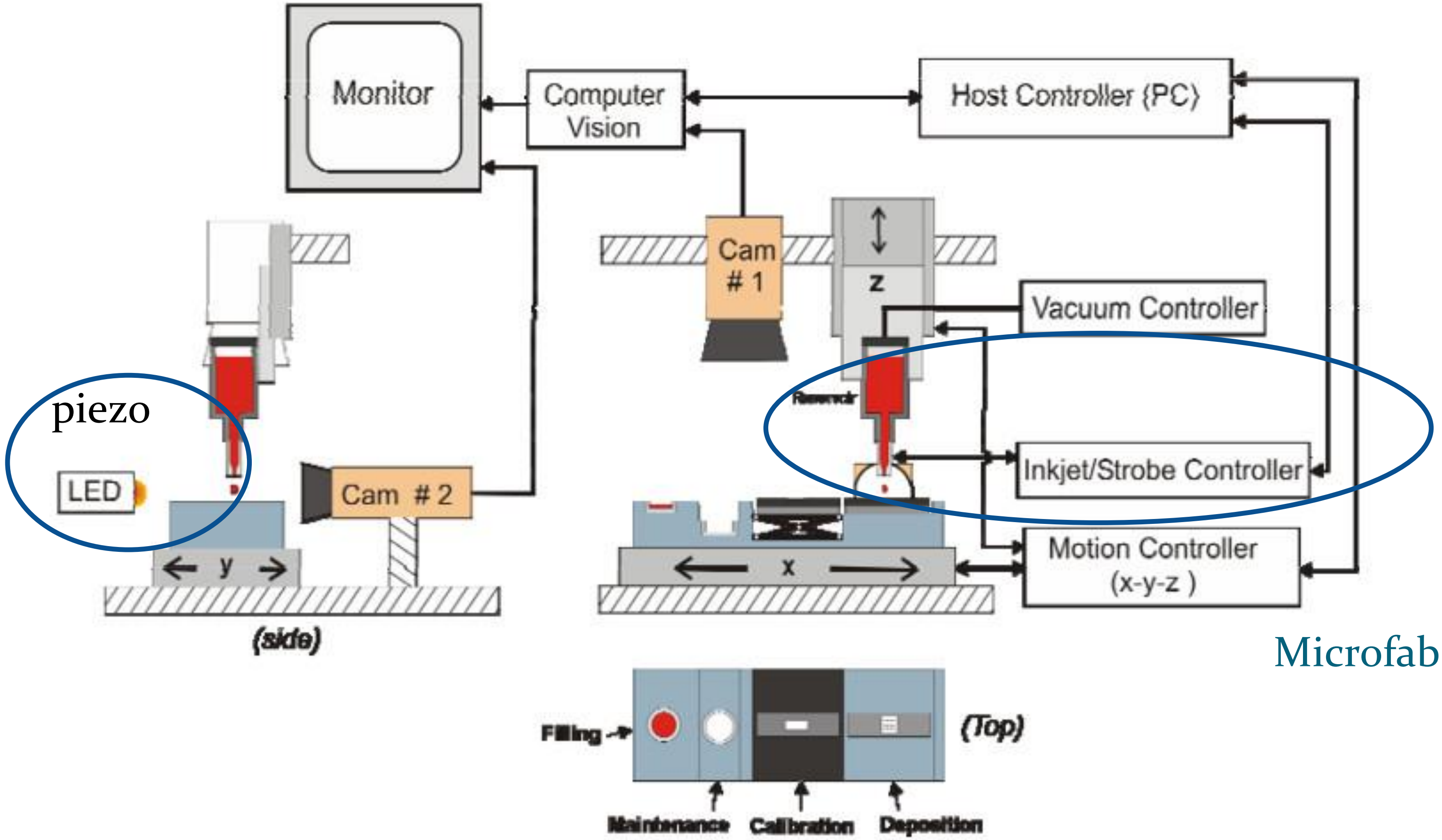
Gen IV



Gen V

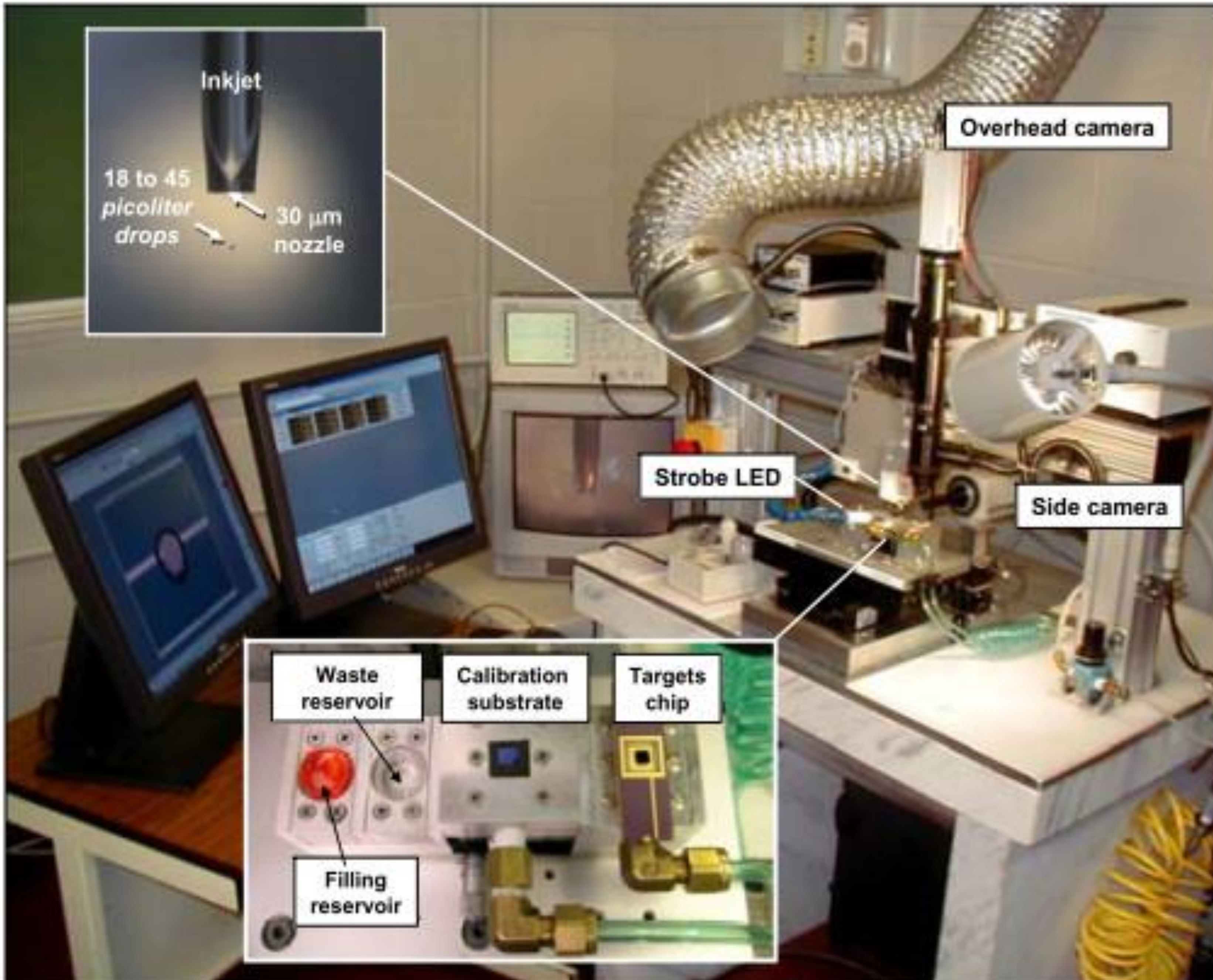


Inkjet

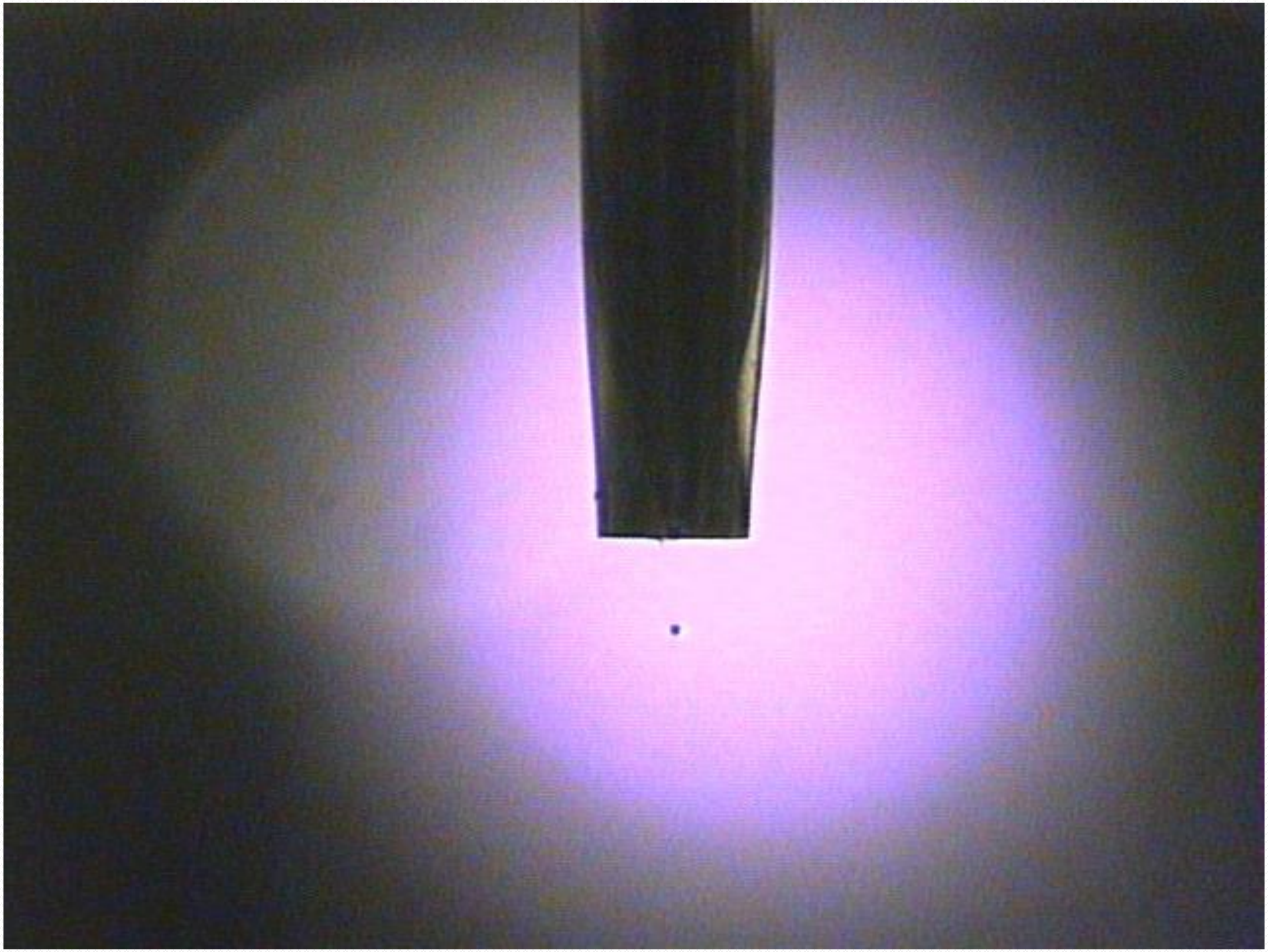


Microfab Inc.

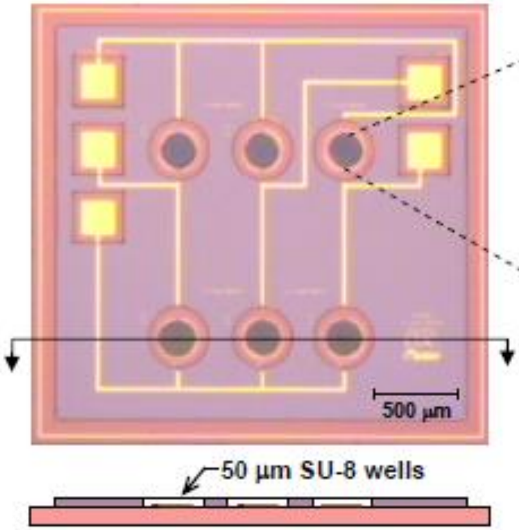
Weiss, Schultz and Miller CMU-RI-TR-06-15V2,2006

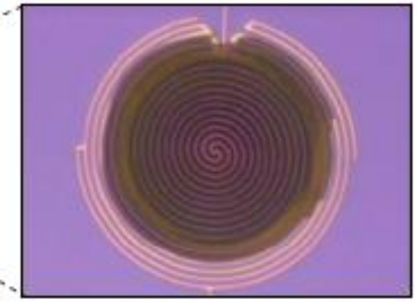

Inkjet
18 to 45
picoliter
drops
30 µm
nozzle
Overhead camera
Strobe LED
Side camera
Waste
reservoir
Calibration
substrate
Targets
chip
Filling
reservoir

A "frozen in space" drop from a 30 μm nozzle

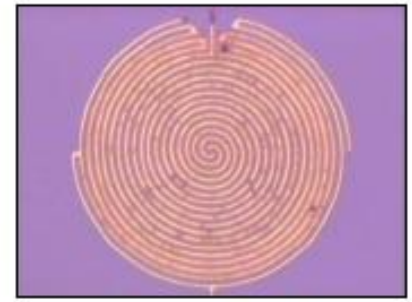


- Droplet volume:
    - 14 pl (aqueous inks)
    - 45 pl (organic solvents)
- Accurate deposition (4 μm)
- Deposition into 3D features
- Thin films (~ 50 to 80 nm thick)
- Wide range of materials: *polythiophenes, nanoparticles, bioinks*

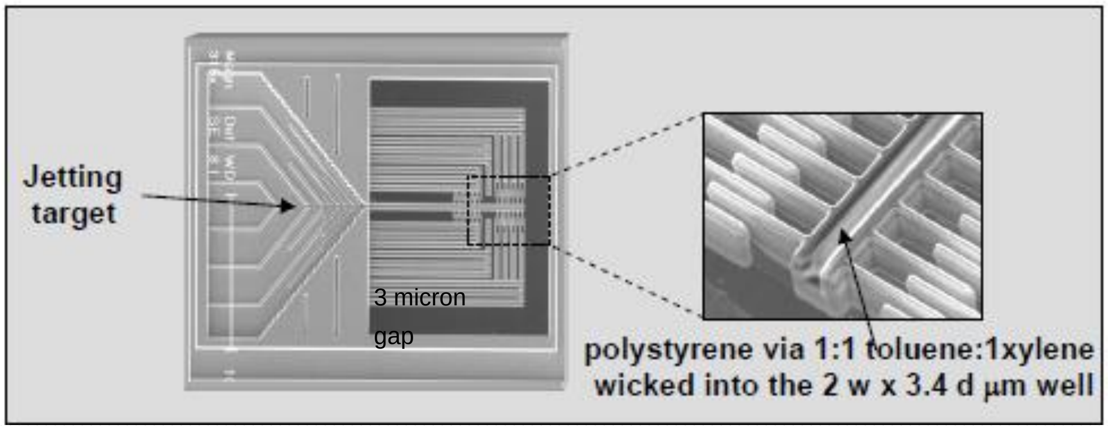


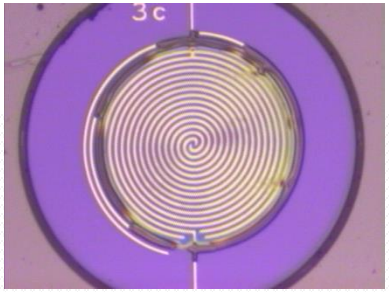


e.g., napthol-terminated poly(3 hexylthiophene

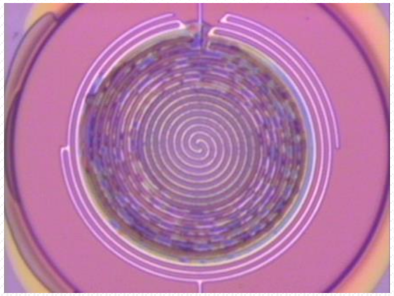


e.g., NRL C8

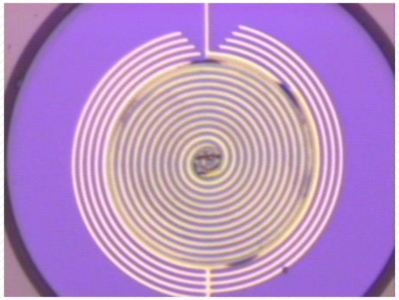




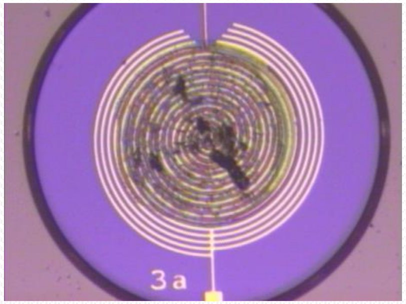
NRL C2C6



SC 403 in NMP

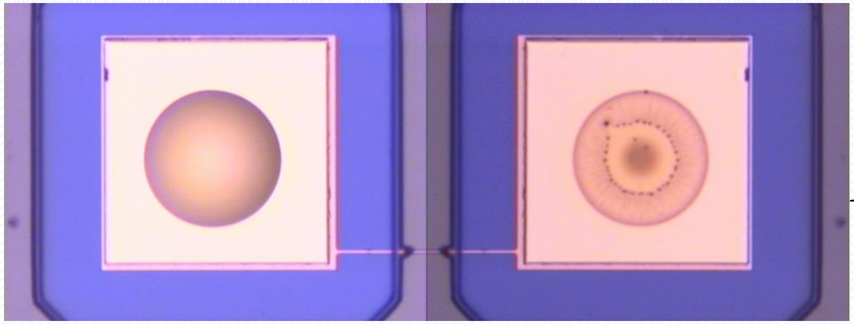


CMU C6



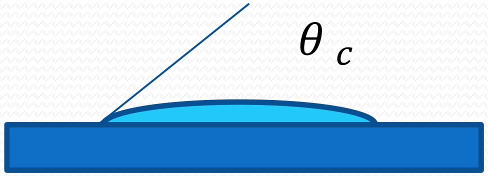
+ 1-thiol undecanoic acid

Wet and dry 1 drop splats on gold.

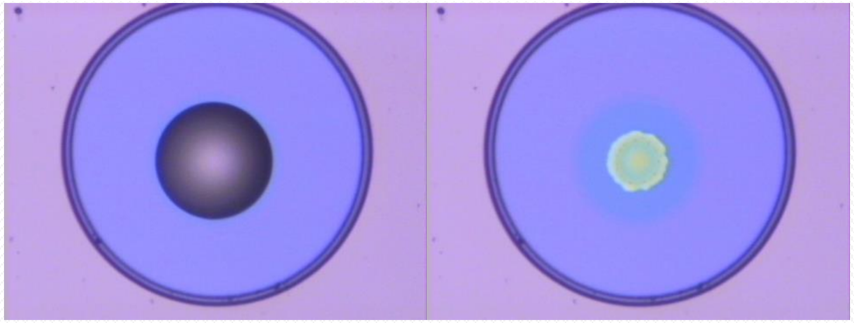


CMU AuC8 10 mg/ml in TCB

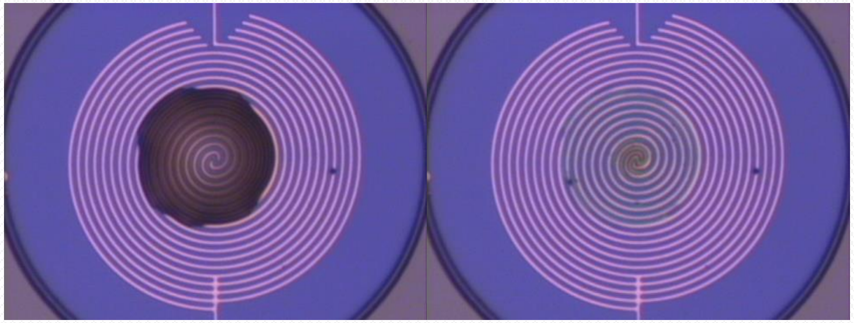
$$D_f = d_0 \sin\theta_c \left(\frac{1}{(3 - 2\sin^2(\theta_c/2))\sin^4(\theta_c/2)} \right)^{\frac{1}{3}}$$



Wet and dry 1 drop splats on SiO2.



Wet and dry 1 drop splats on the electrode.

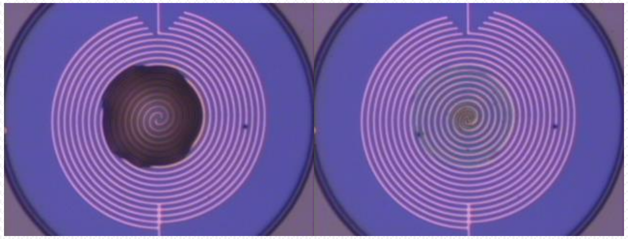


	Number of Drops	Wet Volume, pl	Wet Diameter, microns	Contact Angle
Gold	1	40	112	14
SiO_2	1	40	98	21
Electrode	1	40	112	14
“	4	160	157	20

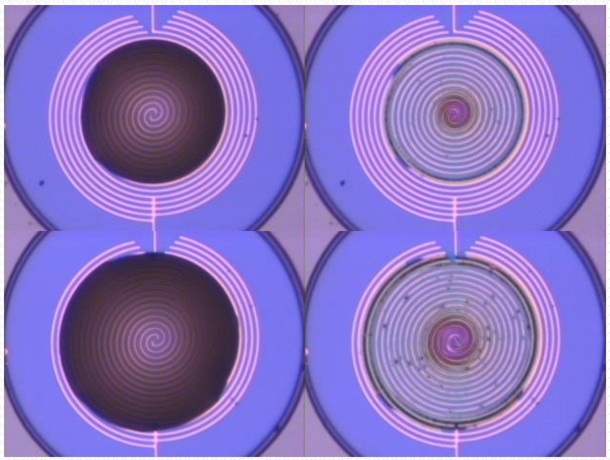
Ink-jet coating of circular electrodes

CMU AuC8 10 mg/ml in TCB

wet dry

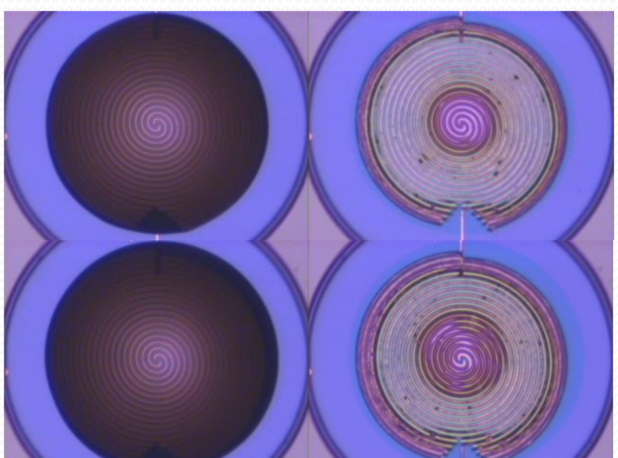


1 drop



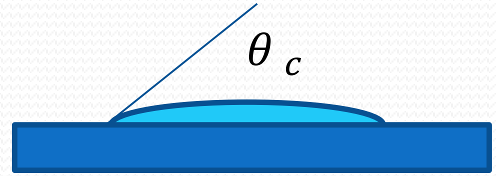
4 drops

8 drops



16 drops

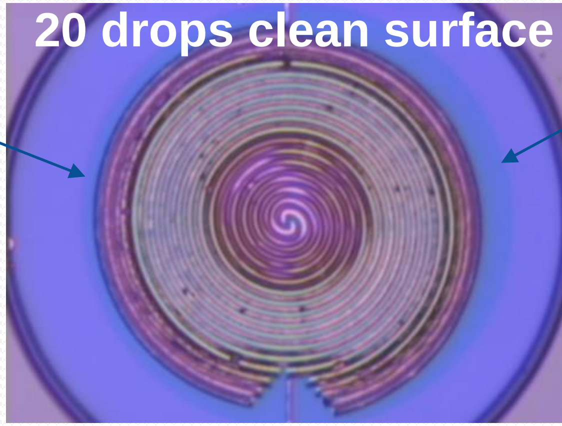
20 drops



$$D_f = d_0 \sin\theta_c \left(\frac{1}{(3 - 2\sin^2(\theta_c/2))\sin^4(\theta_c/2)} \right)^{\frac{1}{3}}$$

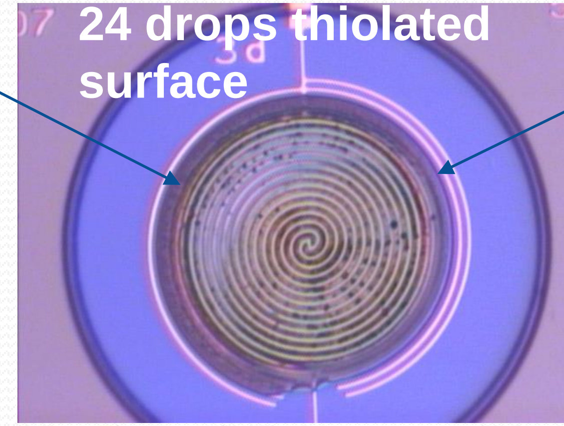
θ_c= 14-21 degrees

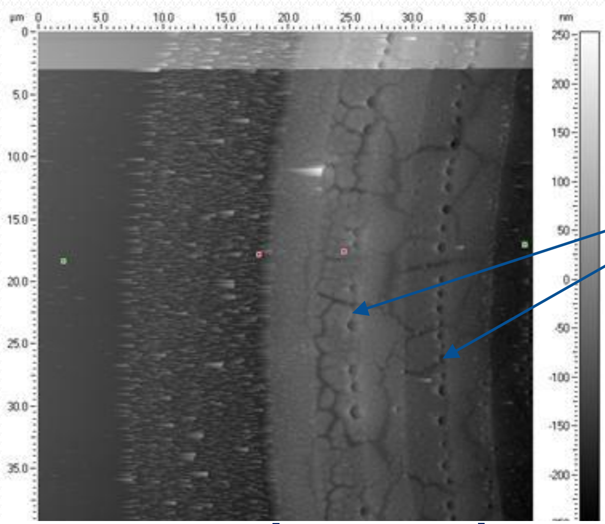
20 drops clean surface



Wet splat edge

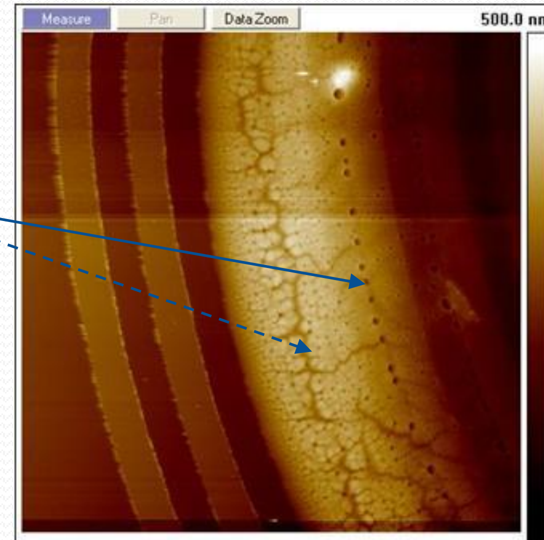
24 drops thiolated surface



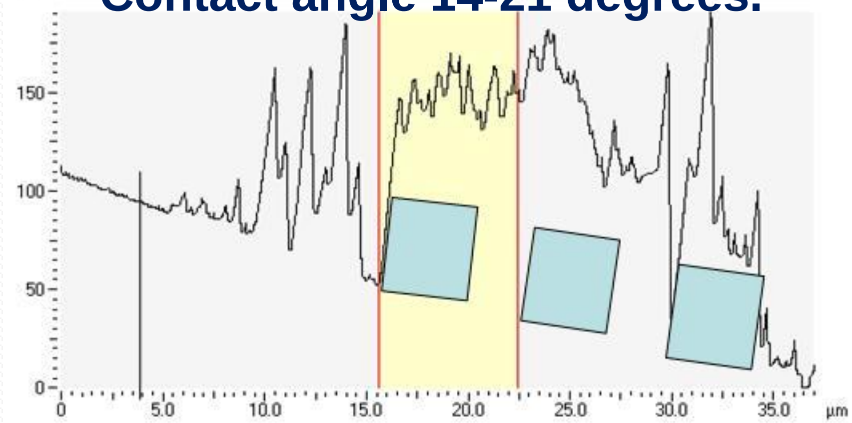


pinholes

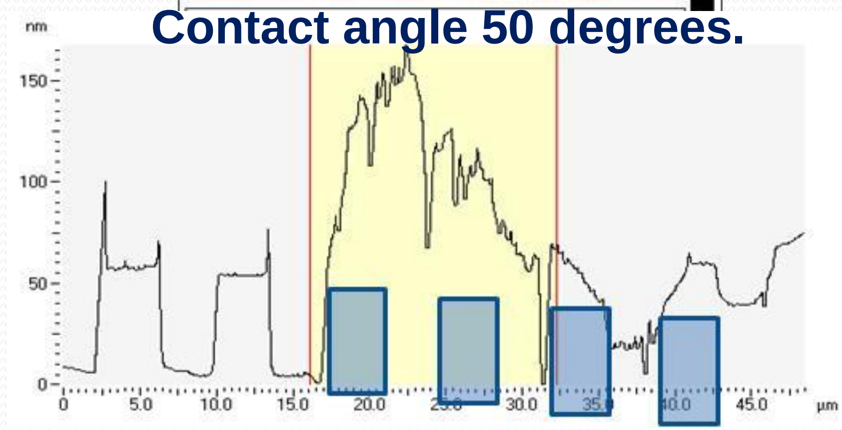
AFM

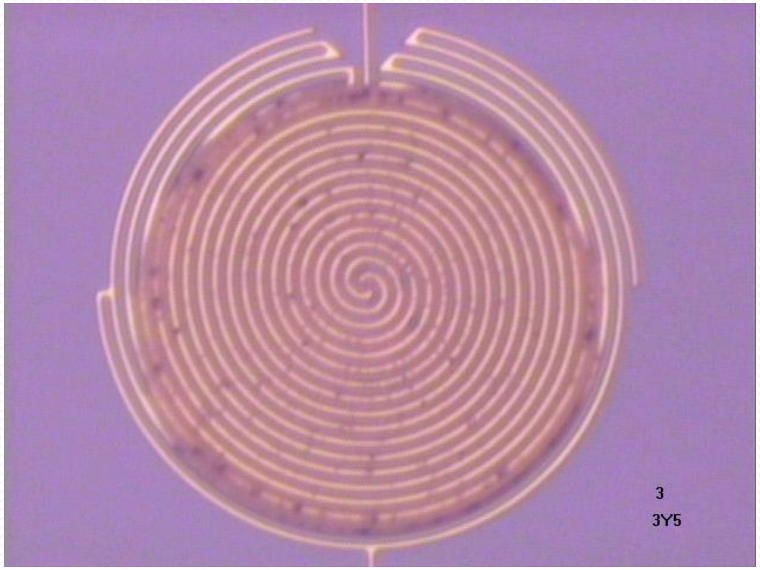


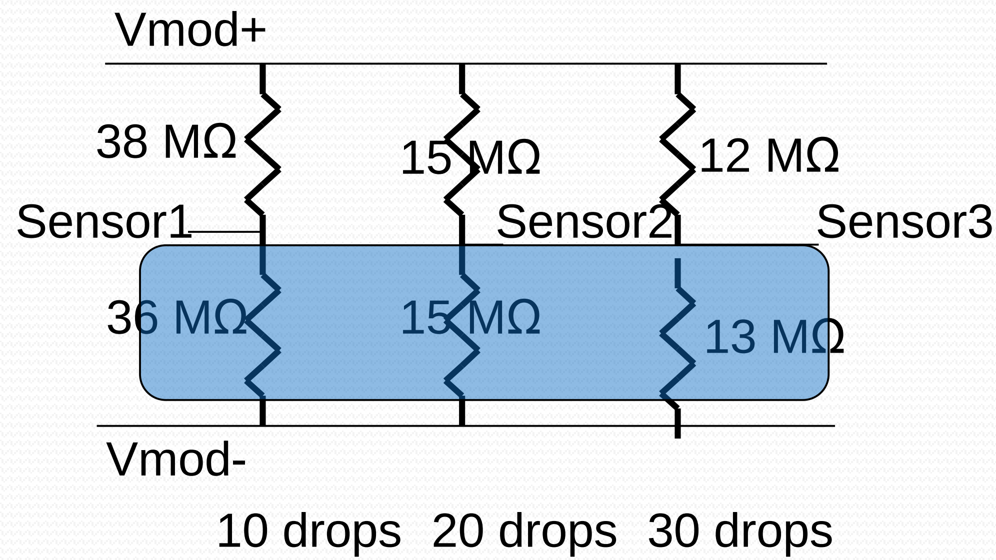
Contact angle 14-21 degrees.



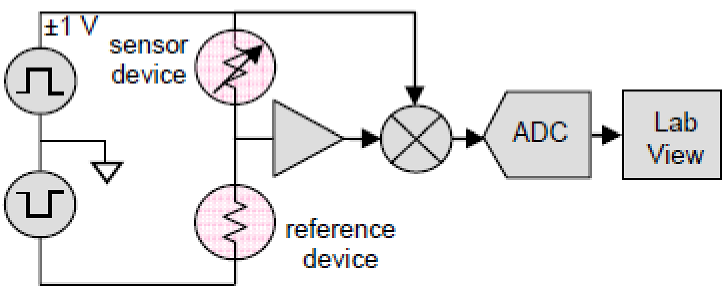
Contact angle 50 degrees.

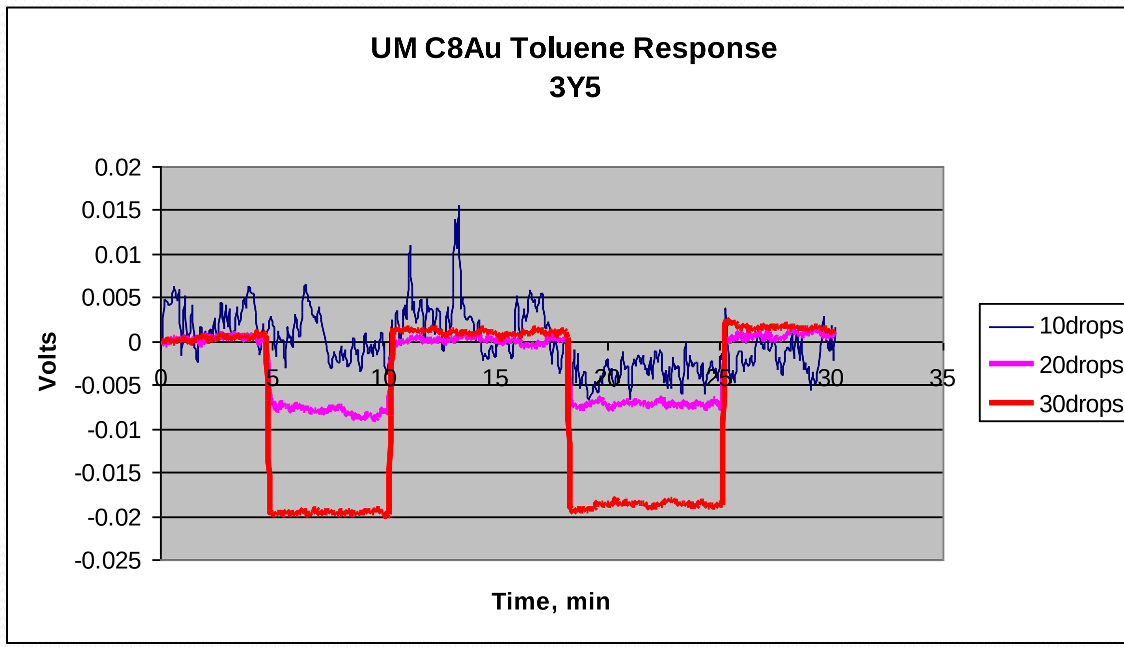


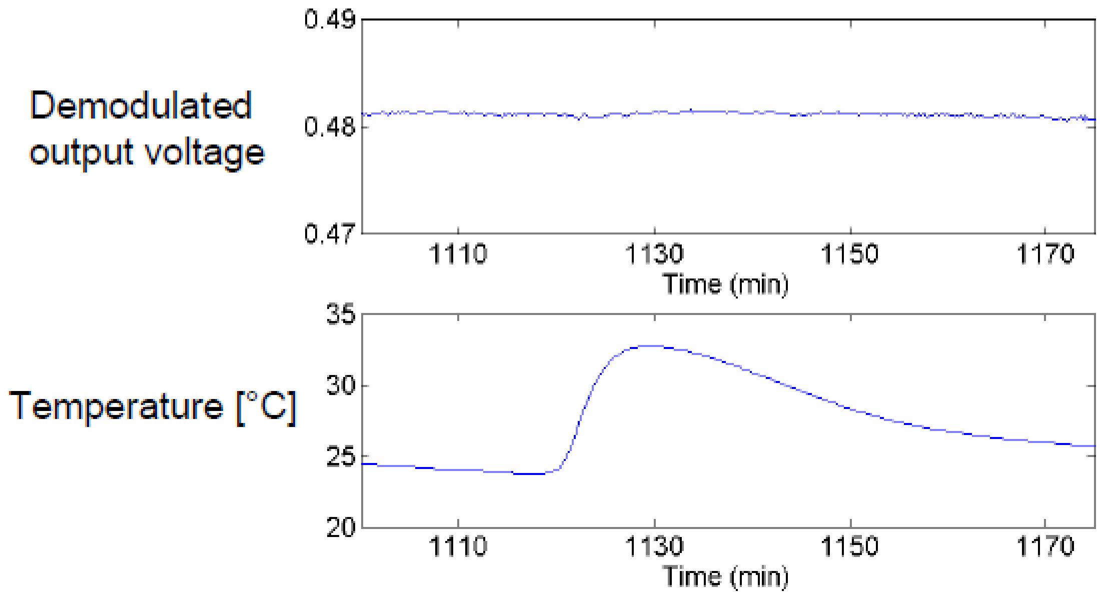




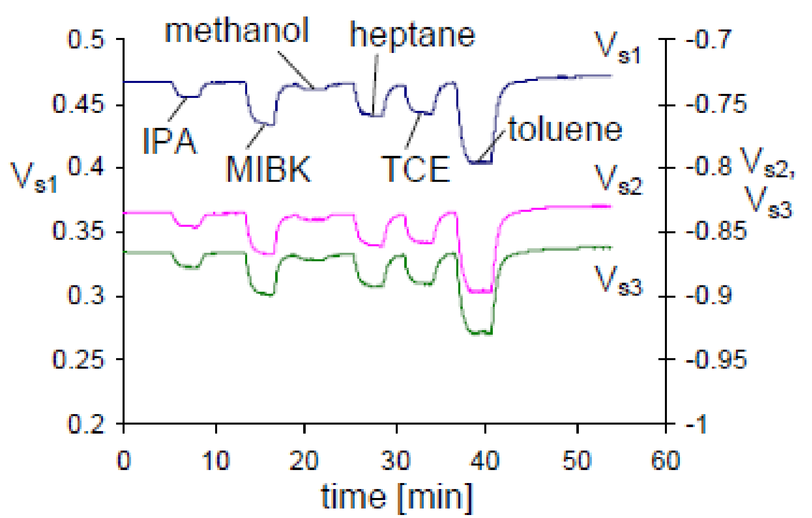
UM C8 (3.6 mg/ml) 30 drops







T response



solvents response

No carbon

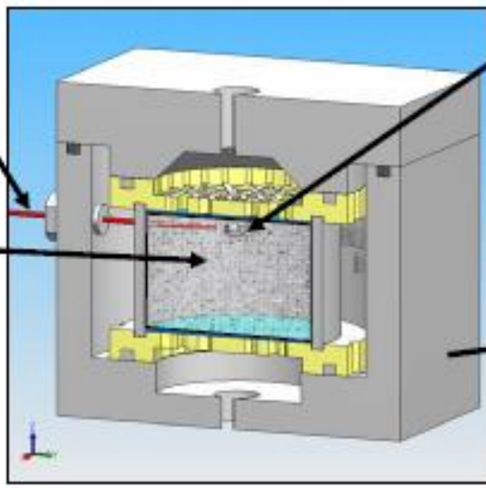
Solvents- 500 ppm
except : methanol 2000 ppm

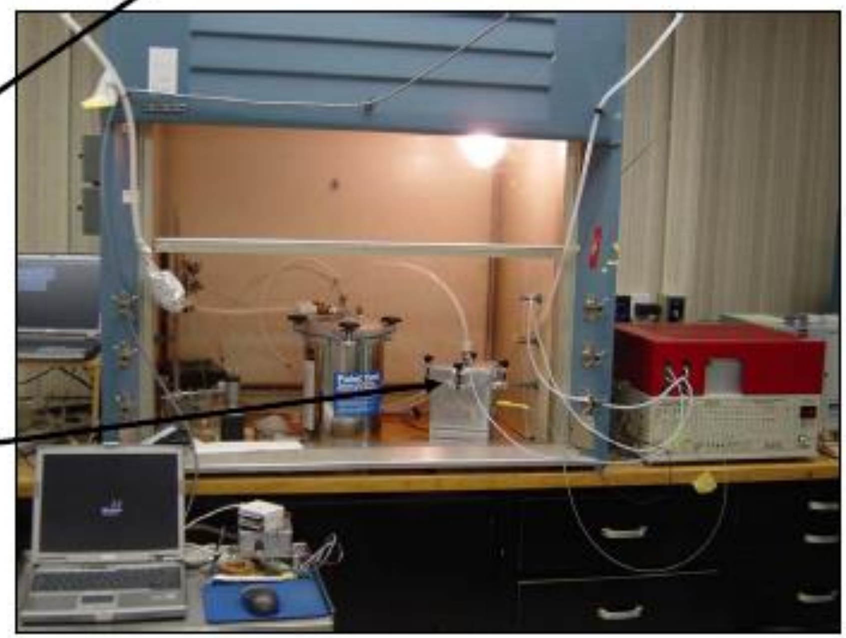
- NIOSH Cartridge Simulator
  - In carbon pack
  - Variable humidity
  - Humidity and analyte
  - Large flows

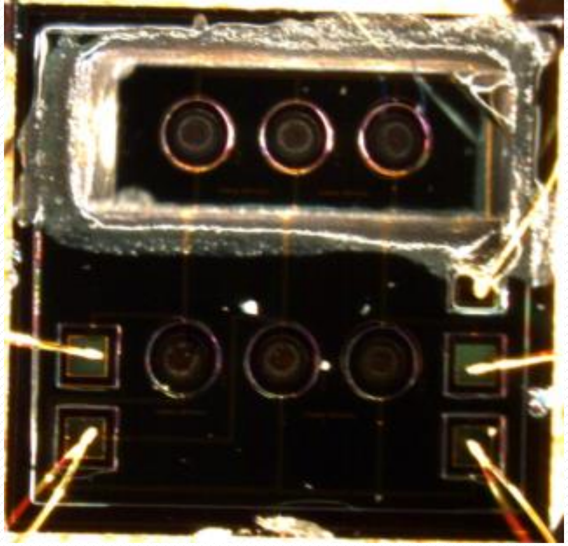
Sensor in TO-5 package, mounted on PC board

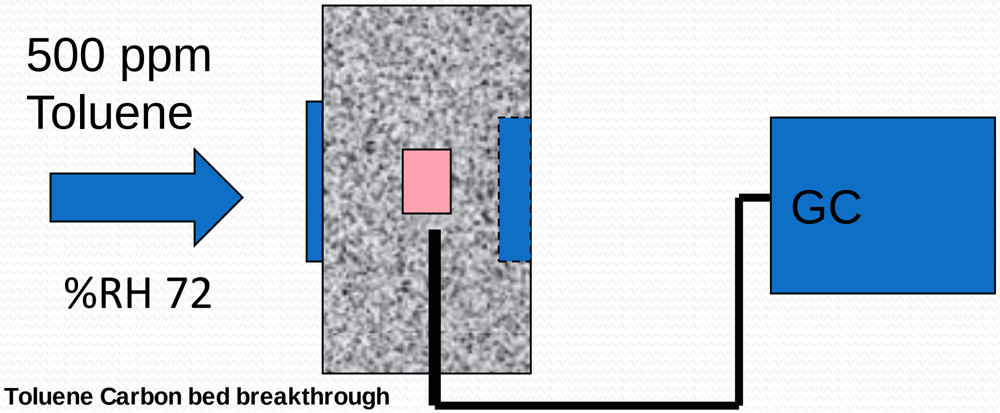
GC sampling

packed carbon bed

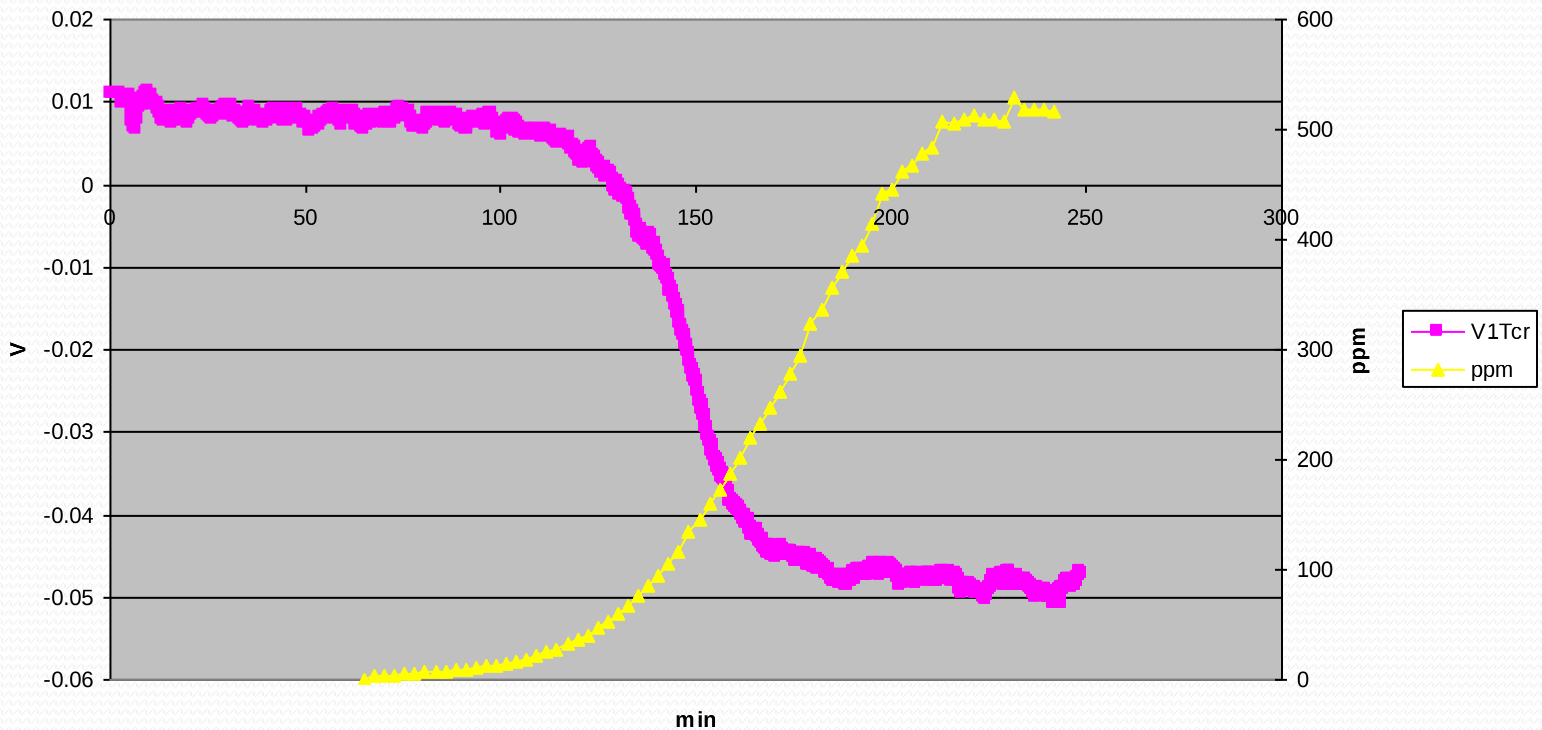






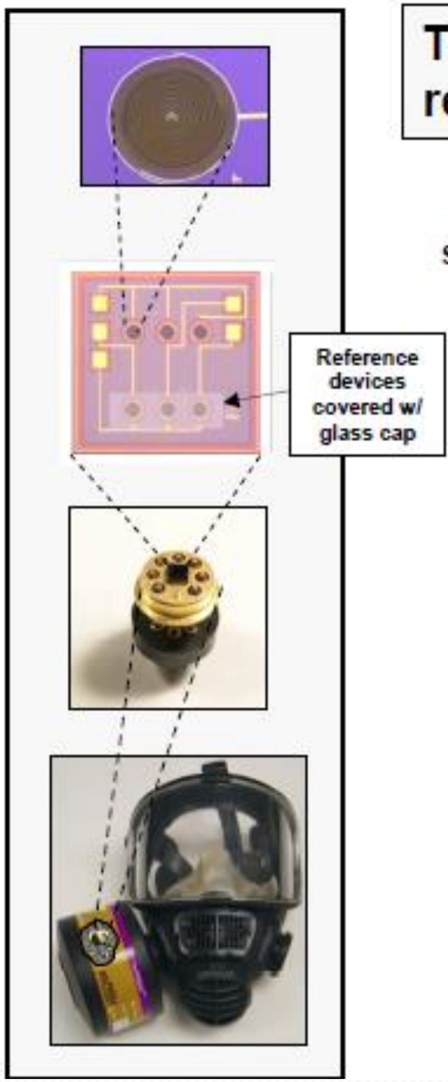


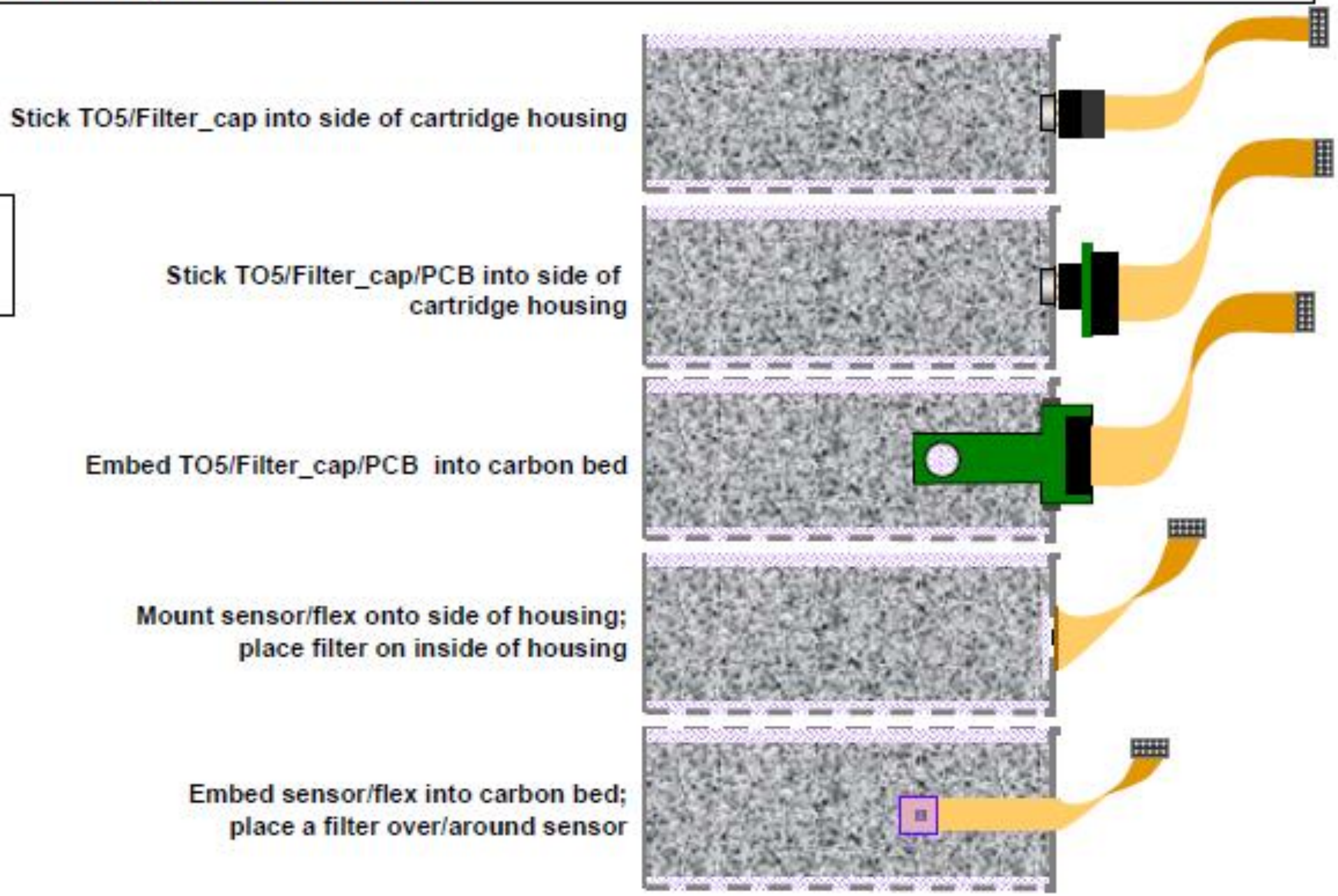
406 CMU C8 150 dr Toluene Carbon bed breakthrough
Arathane-Epoxy
1-4-08



60 mV/ 500 ppm

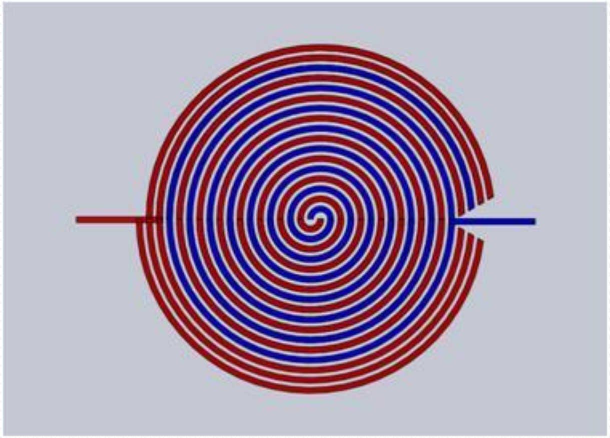
Testing in collaboration with cartridge manufactures has recently been initiated.





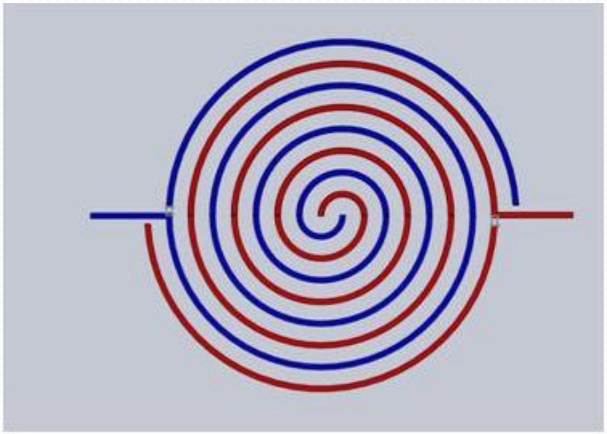
Scaling effects of spiral electrodes

- Is there a preferred and practical gap width for constant area intertwined "spiral" transducers inkjetted with MPC's?

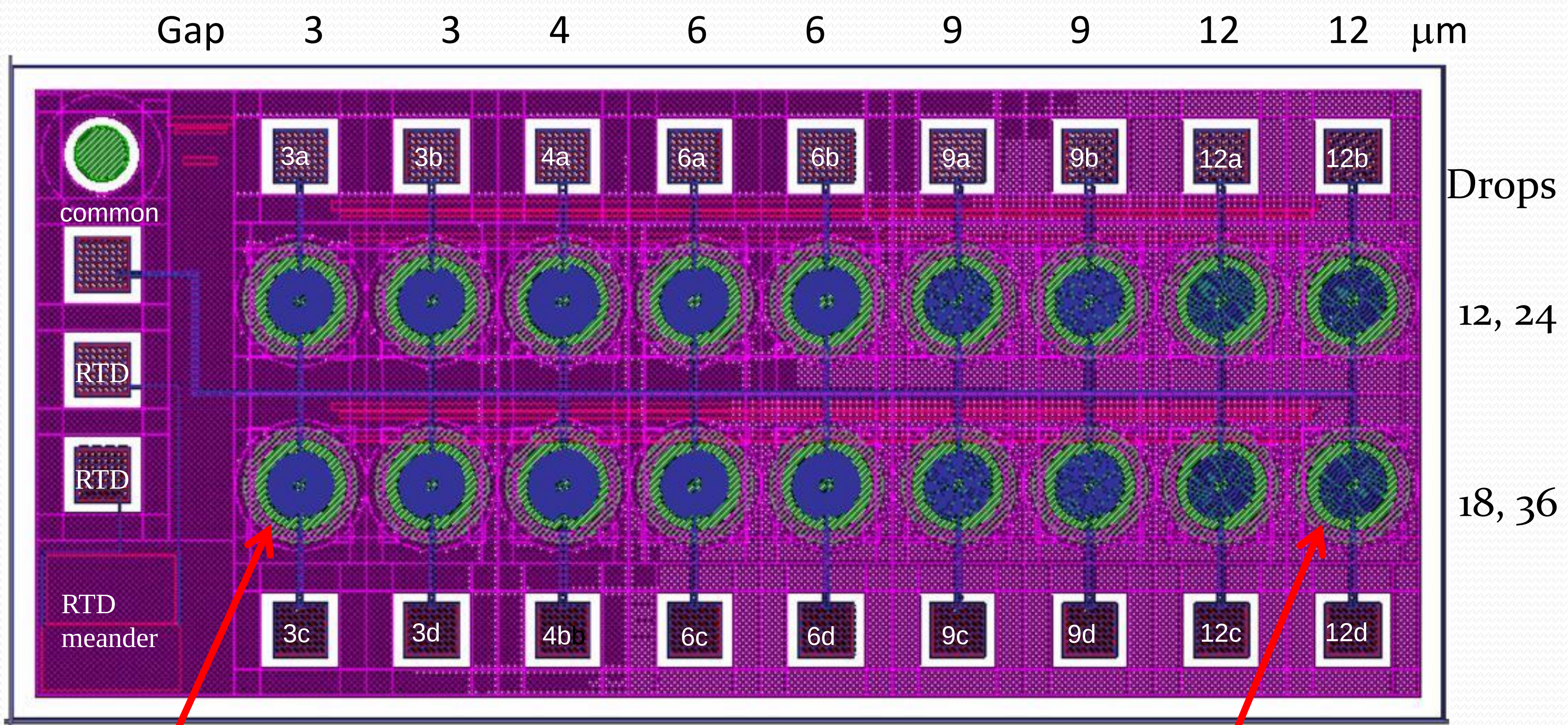


3 micron gap

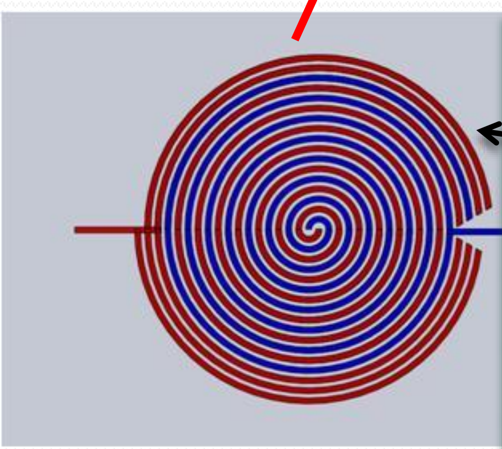
....



12 micron gap

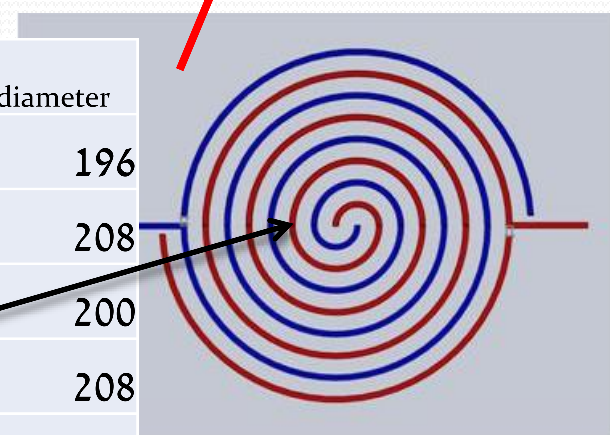


2.5 by 5 mm chip



3 micron gap

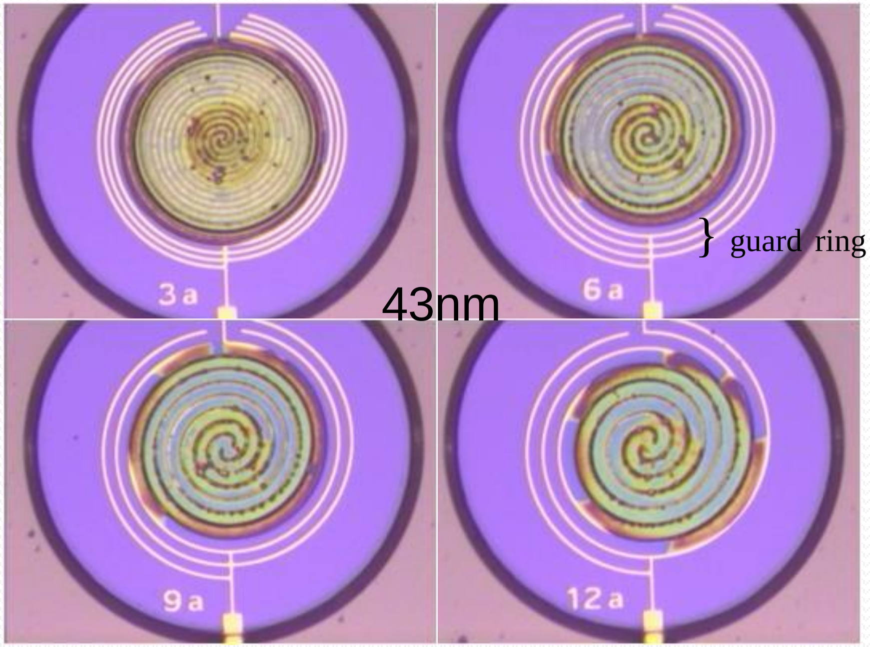
pitch	gap	width	width/gap	diameter
7	**3**	4306	1436	196
8	4	3621	905	208
10	6	3142	524	200
13	9	2611	290	208
16	**12**	2454	204	224



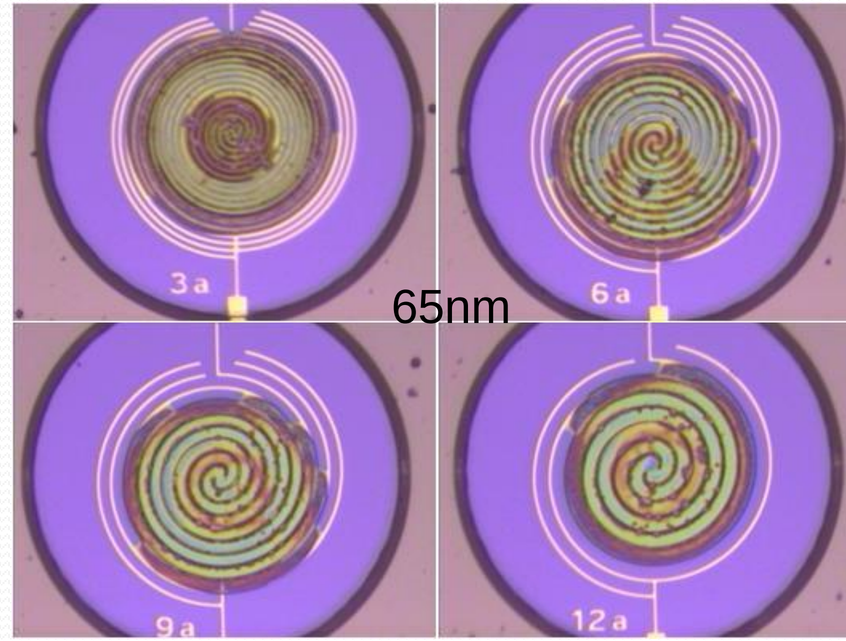
12 micron gap[21]

CMU C8

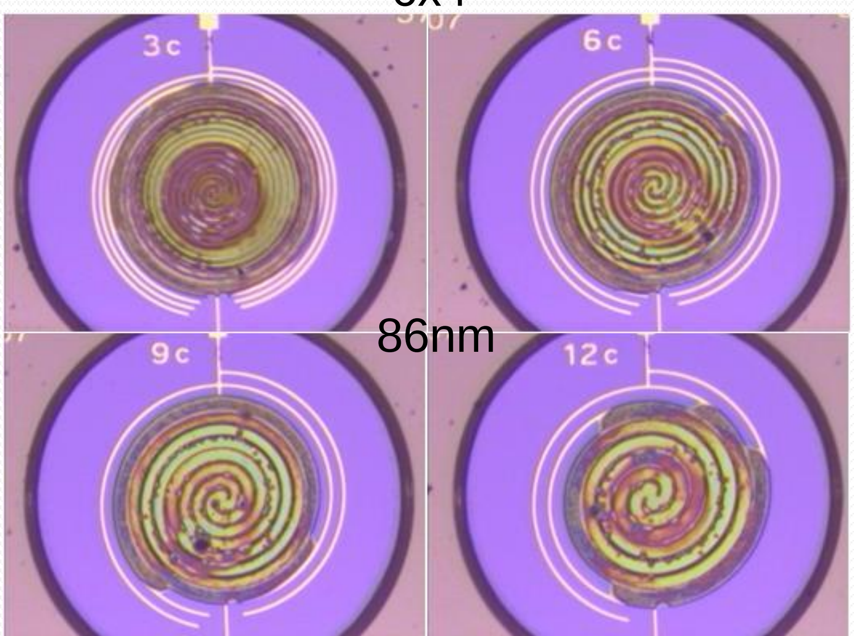
6x2



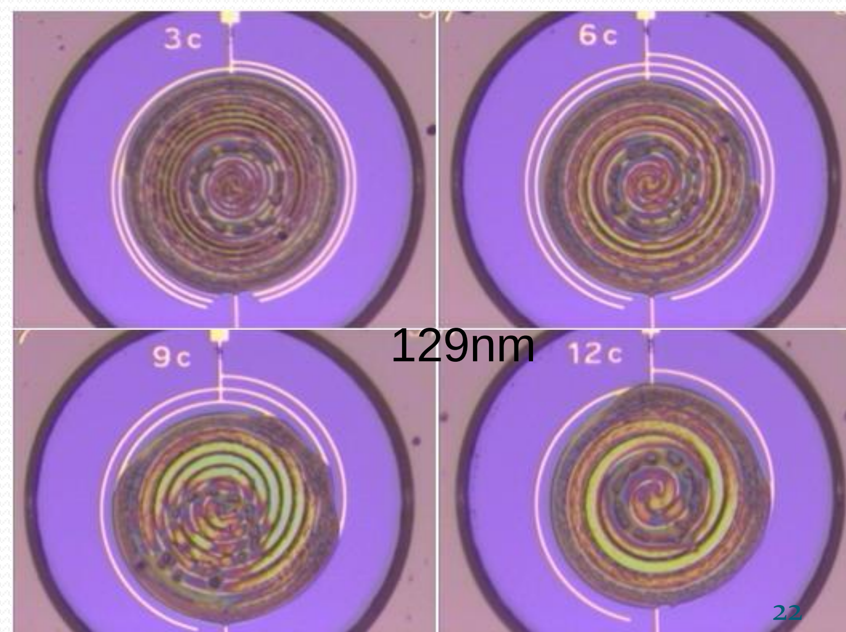
6x3



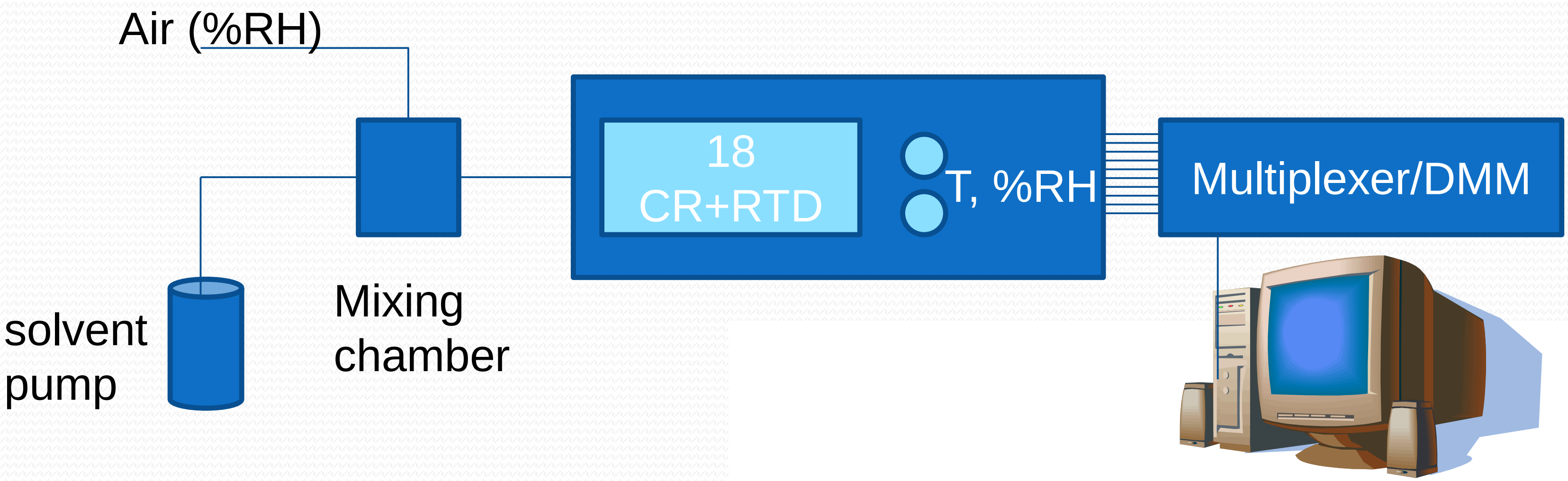
6x4

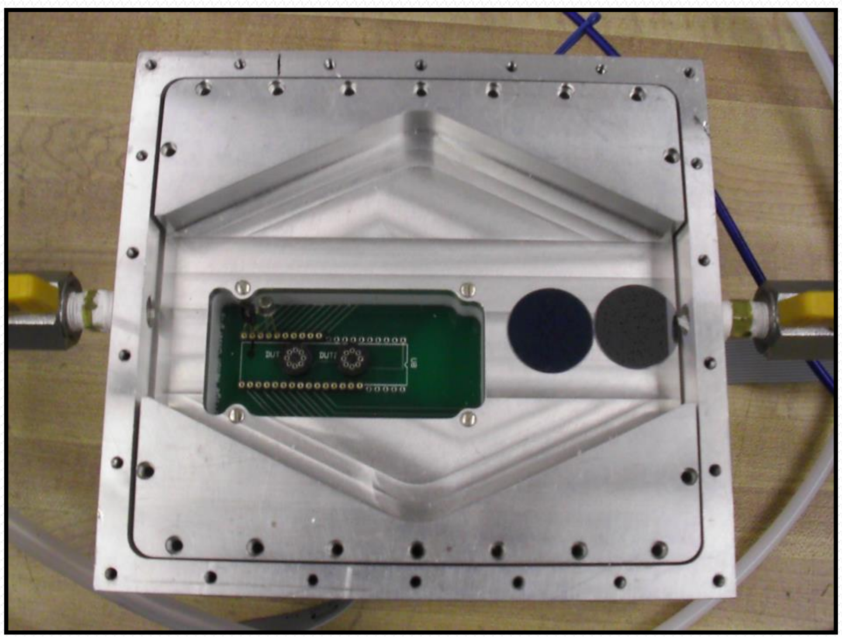


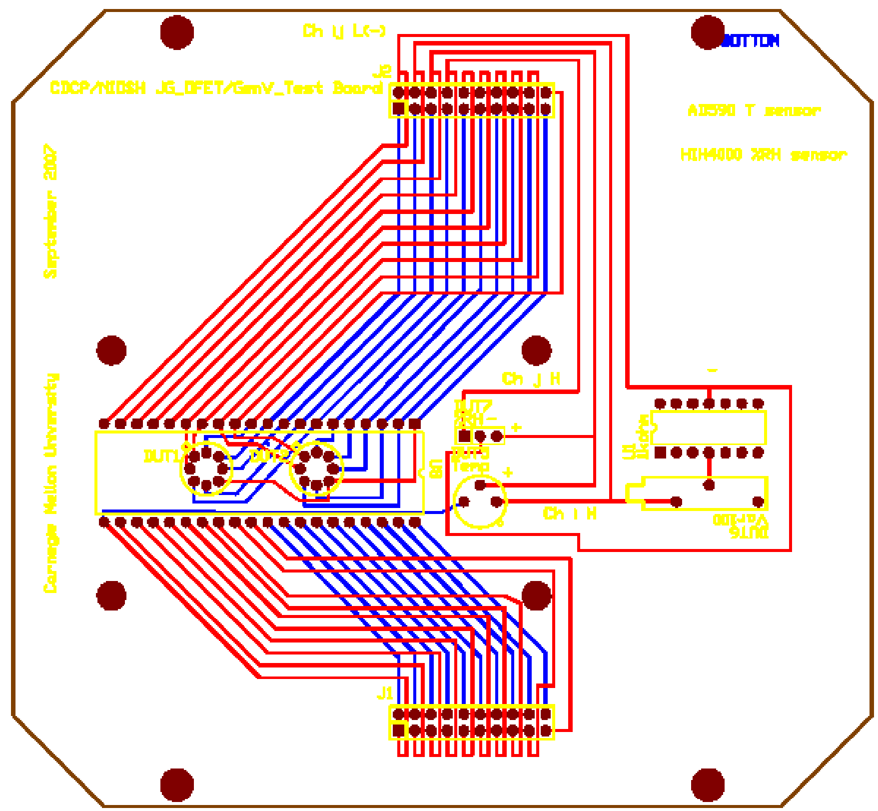
6x6



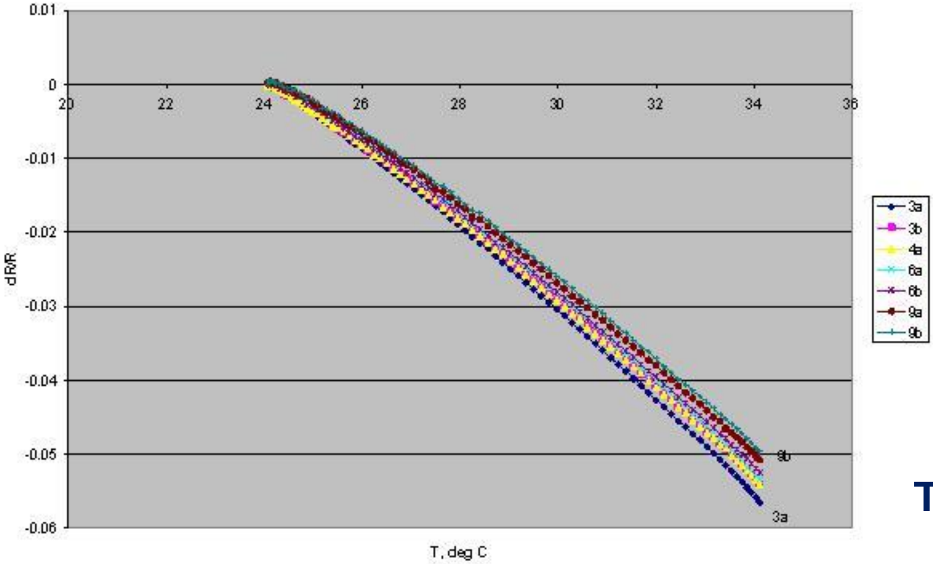
Experimental setup





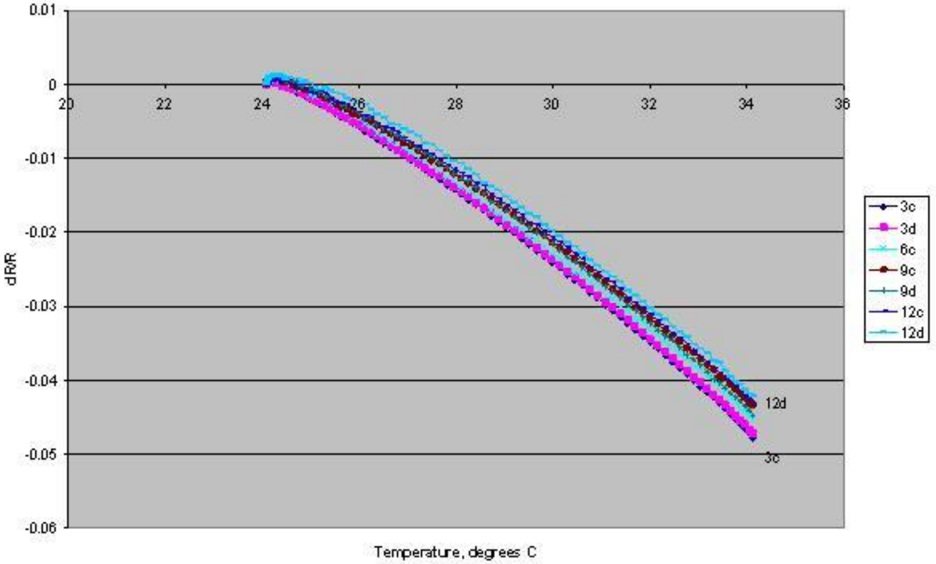


Temperature sensitivity of CMU C8 12 drops

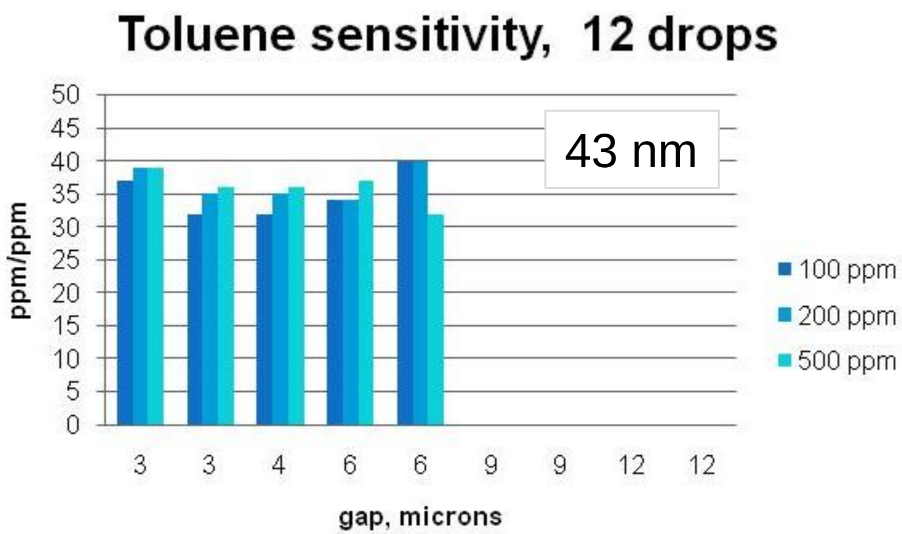


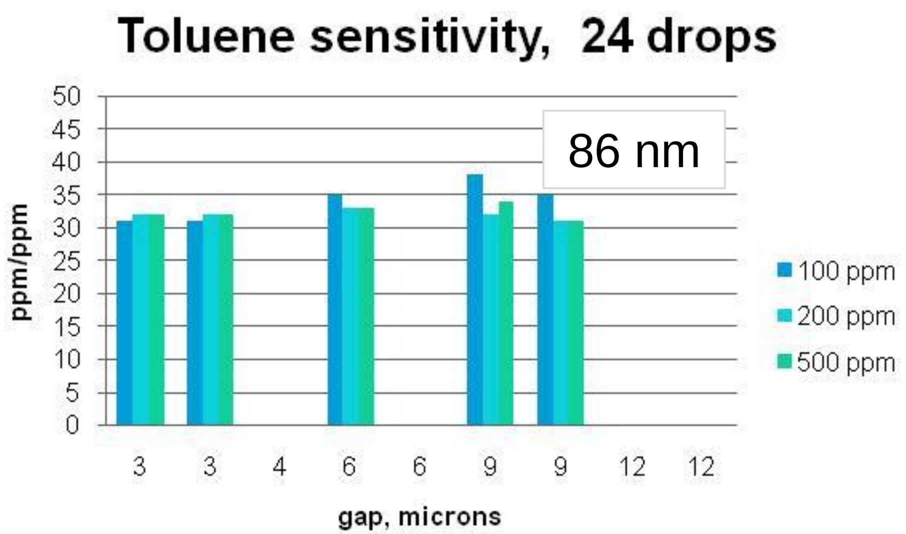
Heatup, 24 to 35 degrees C in 15 min
%RH, 37% to 25%
~5% change per 10 degrees C

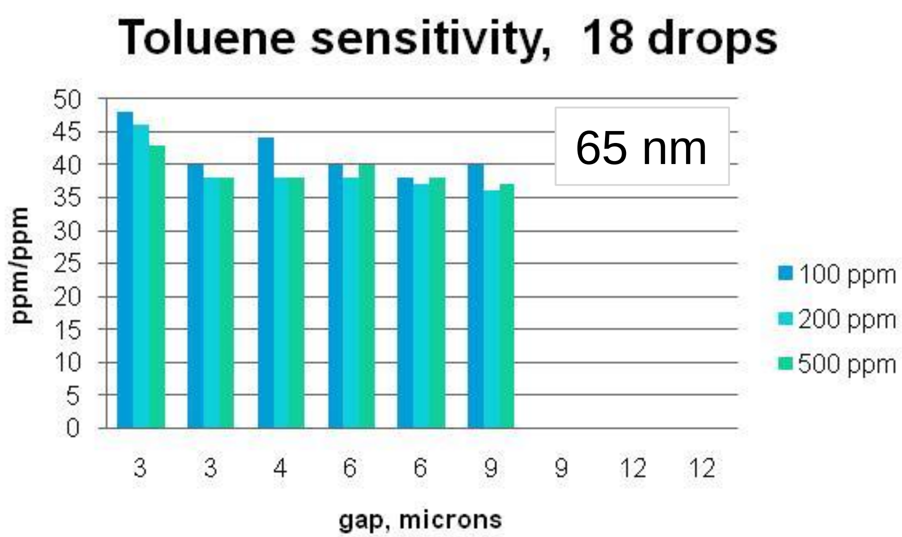
Temperature sensitivity of CMU C8 24 drops

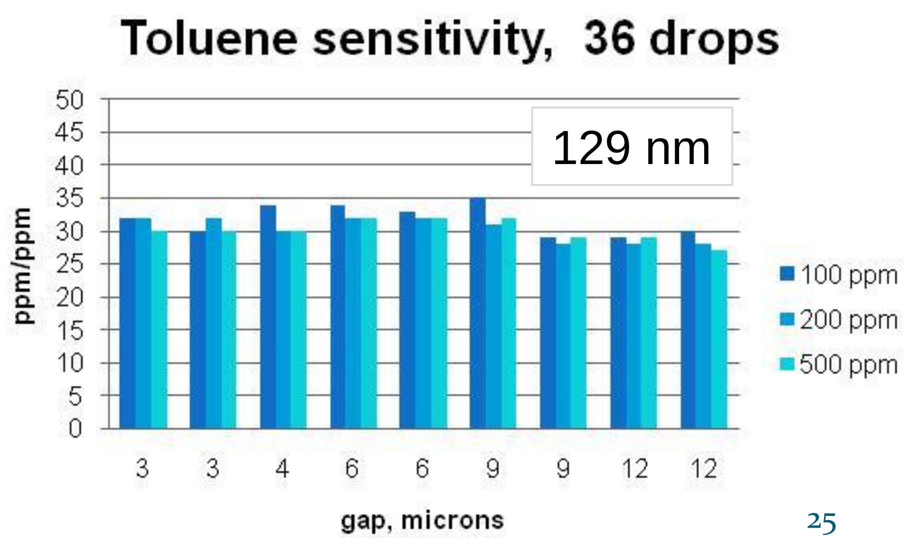


Temperature response is independent on thickness.
Slight dependence on gap width.

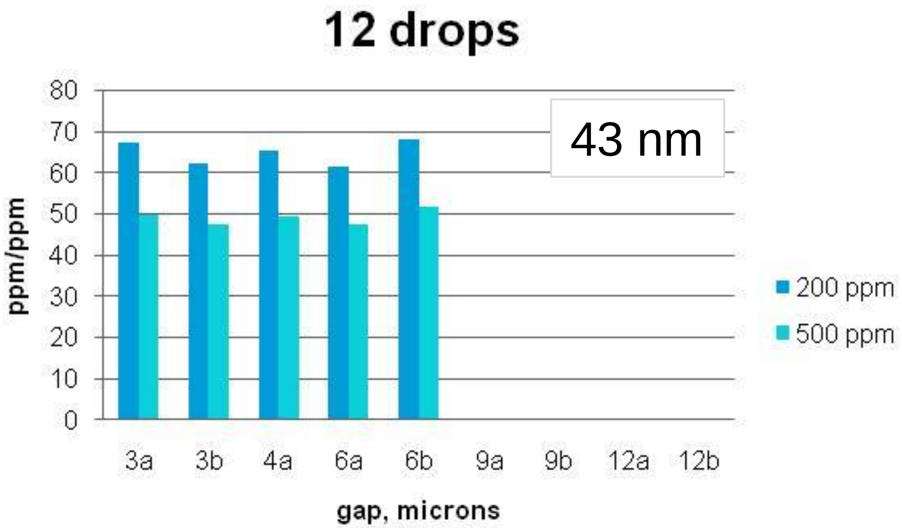

Toluene sensitivity, 12 drops
43 nm
ppm/ppm
50
45
40
35
30
25
20
15
10
5
0
3 3 4 6 6 9 9 12 12
gap, microns
100 ppm
200 ppm
500 ppm

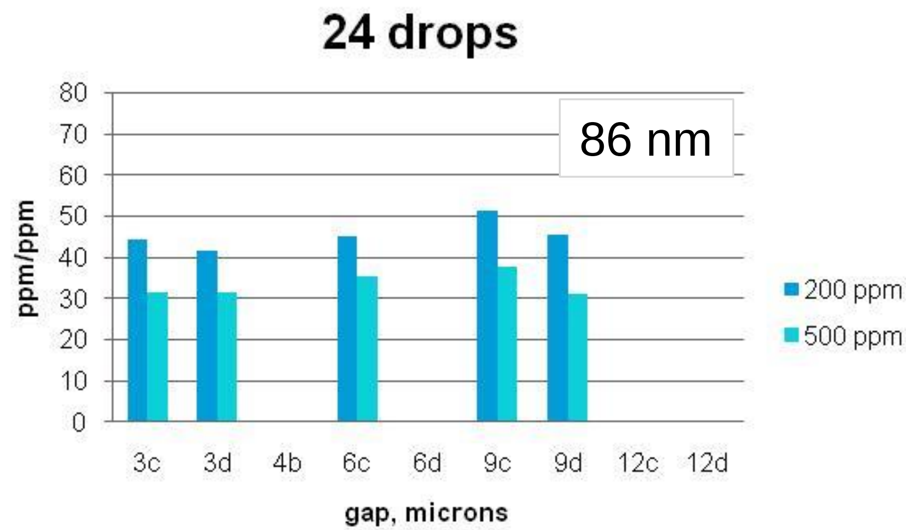

Toluene sensitivity, 24 drops
86 nm
ppm/ppm
50
45
40
35
30
25
20
15
10
5
0
3 3 4 6 6 9 9 12 12
gap, microns
100 ppm
200 ppm
500 ppm

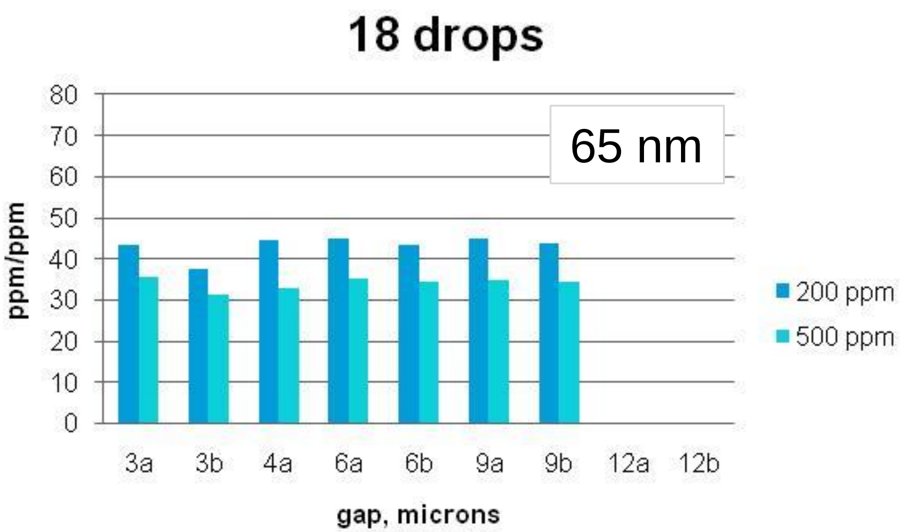

Toluene sensitivity, 18 drops
65 nm
ppm/ppm
50
45
40
35
30
25
20
15
10
5
0
3 3 4 6 6 9 9 12 12
gap, microns
100 ppm
200 ppm
500 ppm

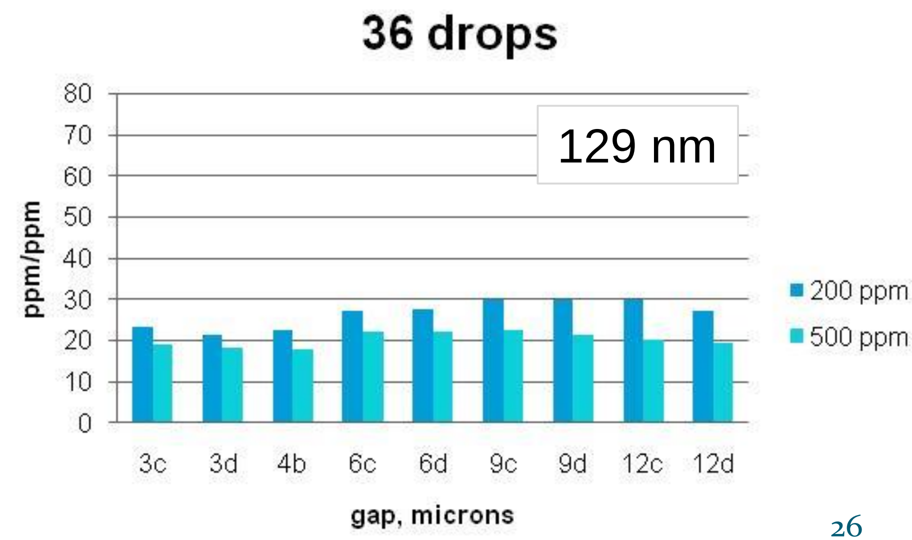

Toluene sensitivity, 36 drops
129 nm
ppm/ppm
50
45
40
35
30
25
20
15
10
5
0
3 3 4 6 6 9 9 12 12
gap, microns
100 ppm
200 ppm
500 ppm

CMU C8 IPA sensitivity

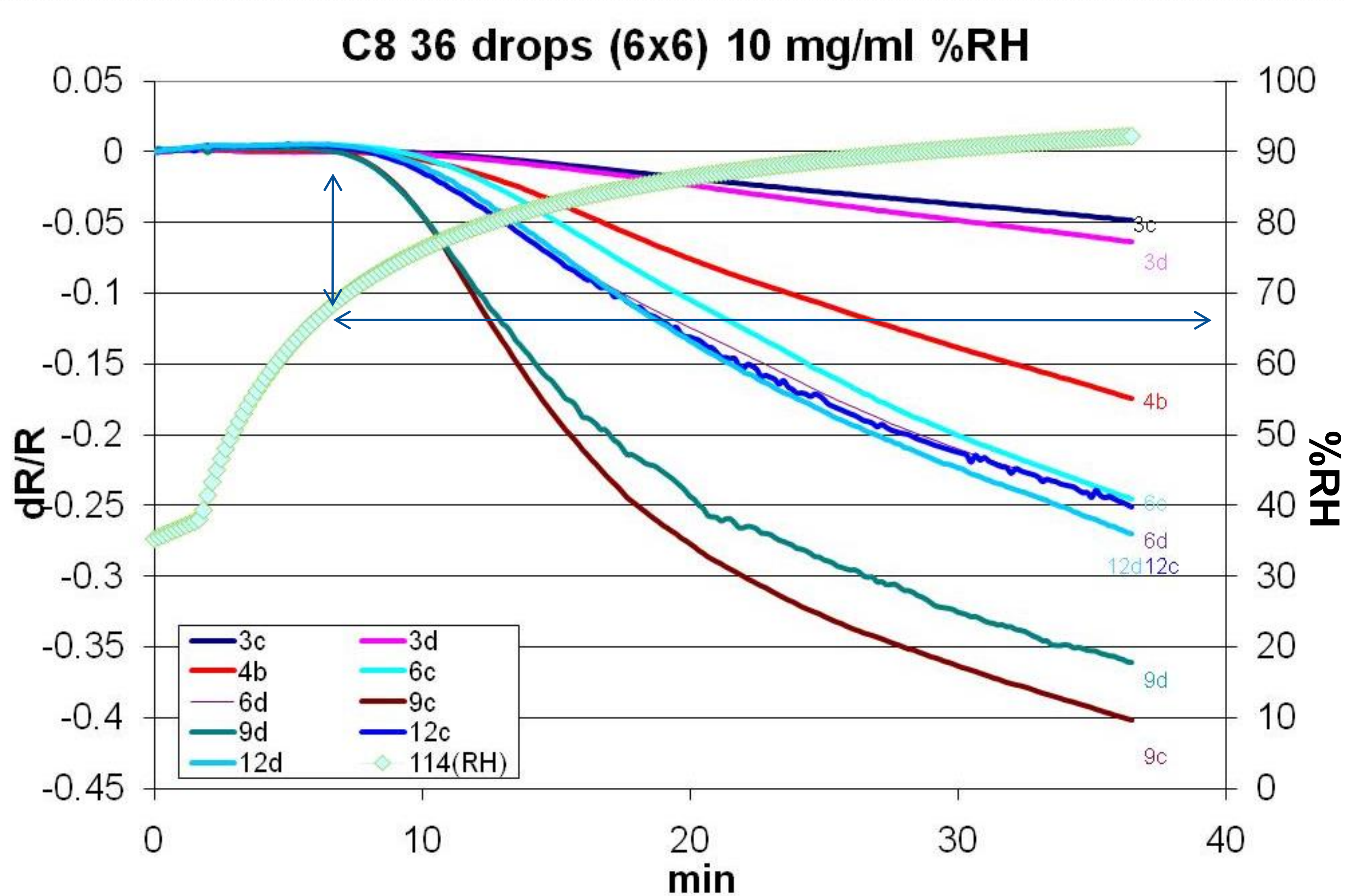




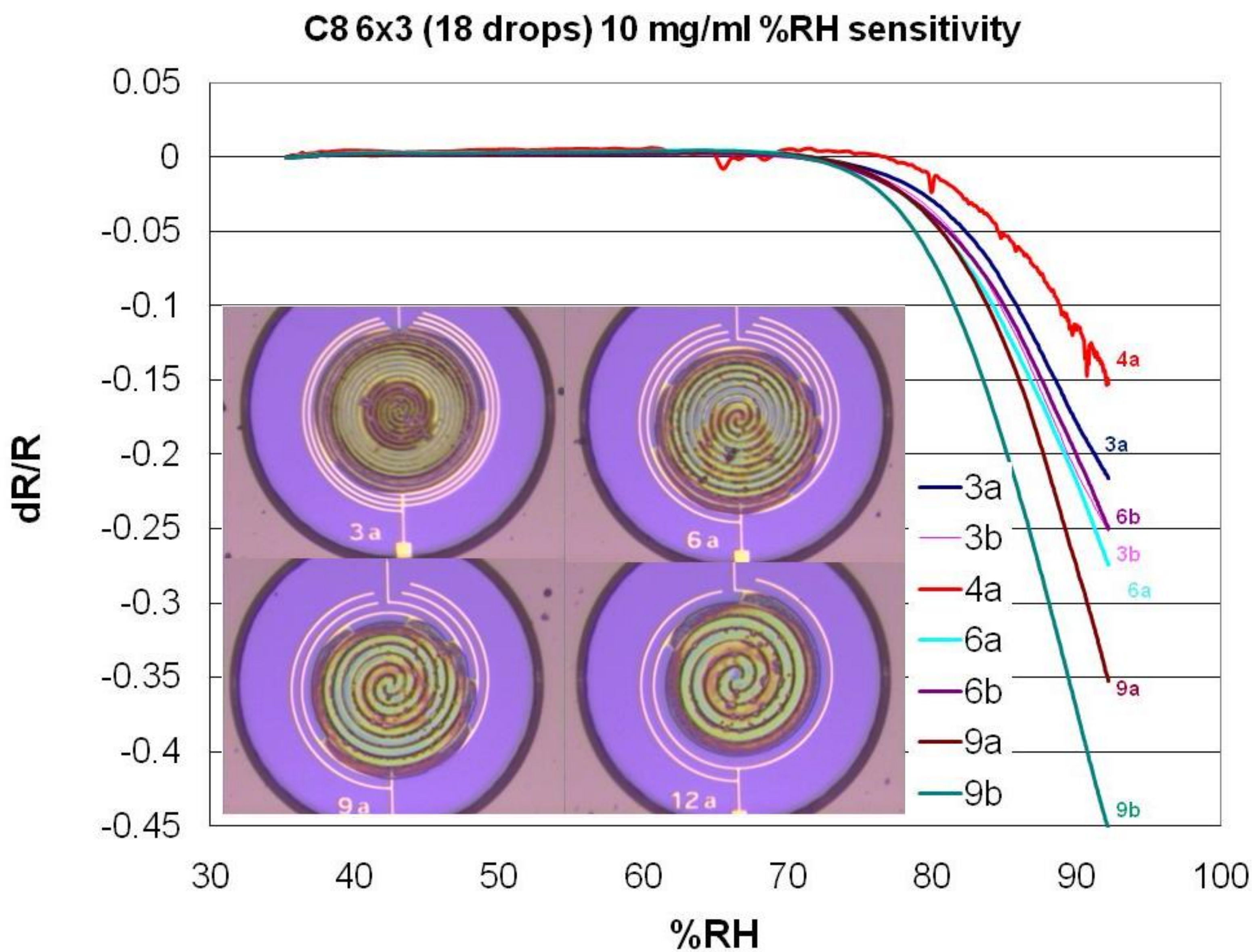




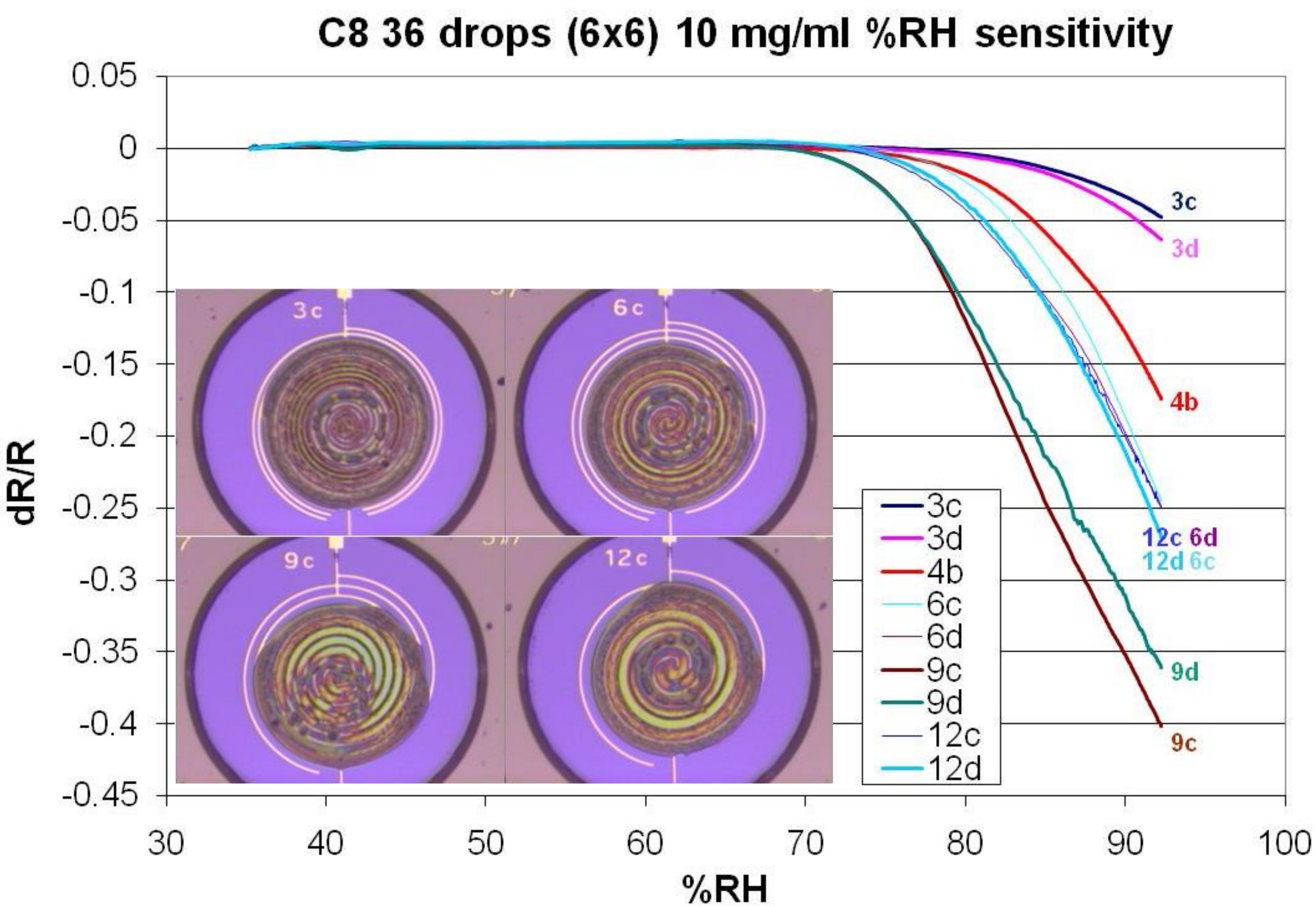
Humidity response is gap dependent for all thicknesses



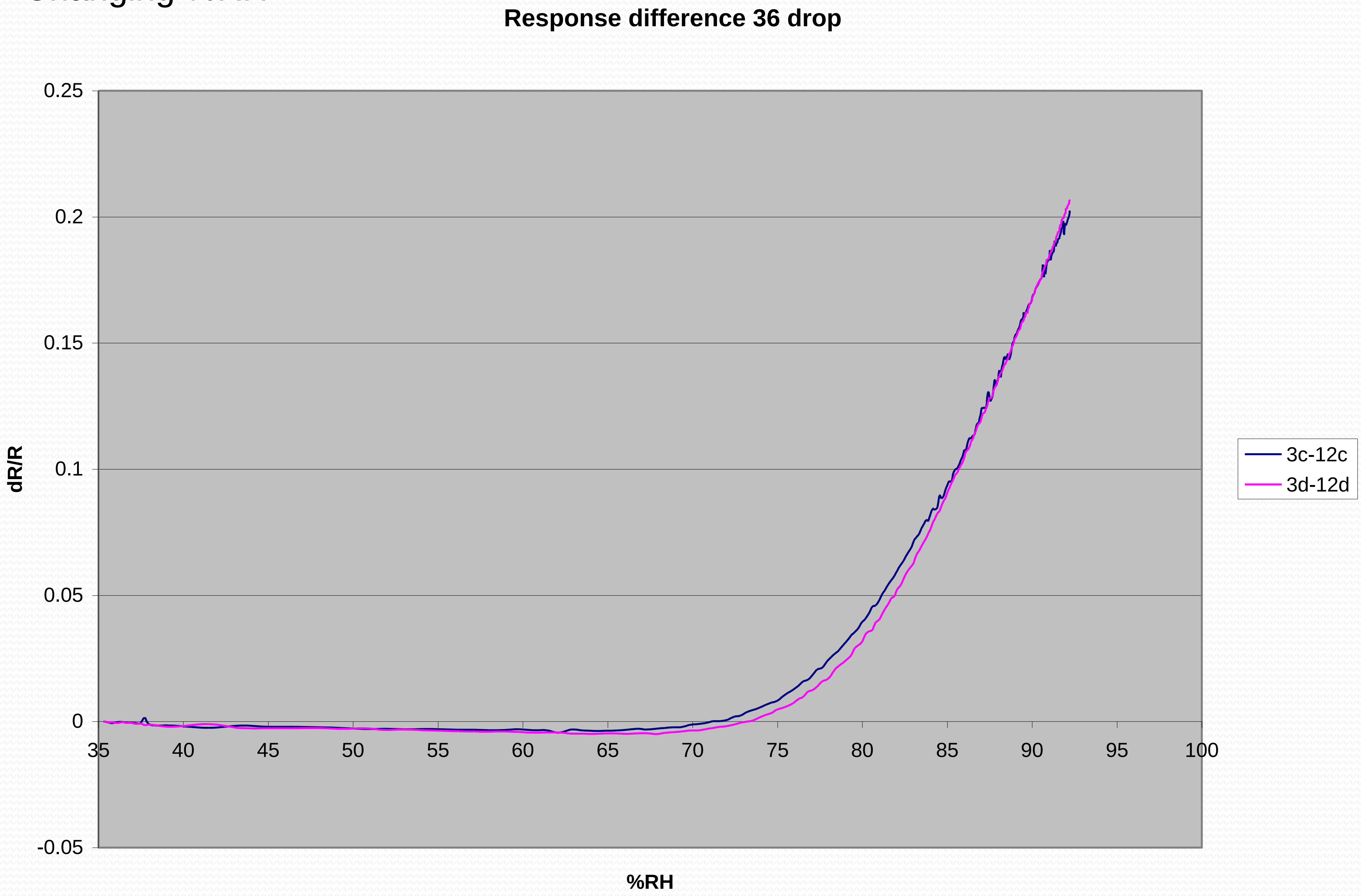
Humidity response is gap dependent for all thicknesses

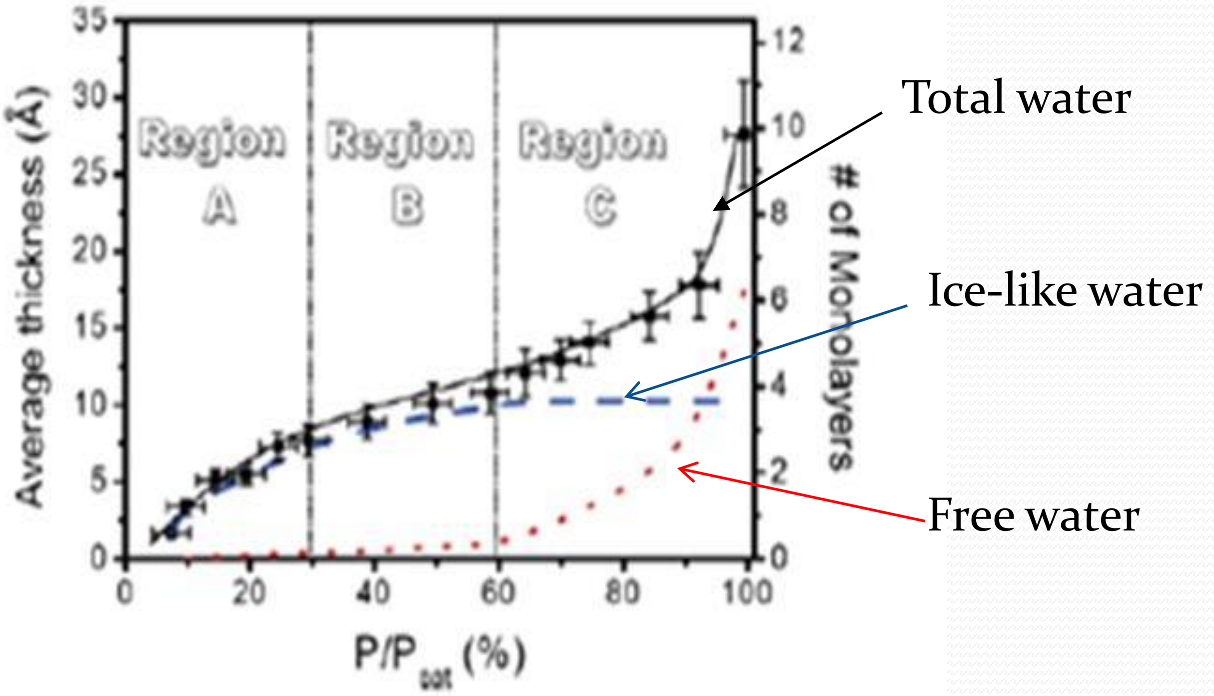

C8 6x3 (18 drops) 10 mg/ml %RH sensitivity
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
-0.35
-0.4
-0.45
dR/R
30
40
50
60
70
80
90
100
%RH
3a
3b
4a
6a
6b
9a
9b
4a
3a
6b
3b
6a
9a
9b
3 a
6 a
9 a
12 a

Humidity response is gap dependent for %RH for all thicknesses



Changing %RH


Response difference 36 drop
dR/R
%RH
0.25
0.2
0.15
0.1
0.05
0
-0.05
35
40
45
50
55
60
65
70
75
80
85
90
95
100
3c-12c
3d-12d



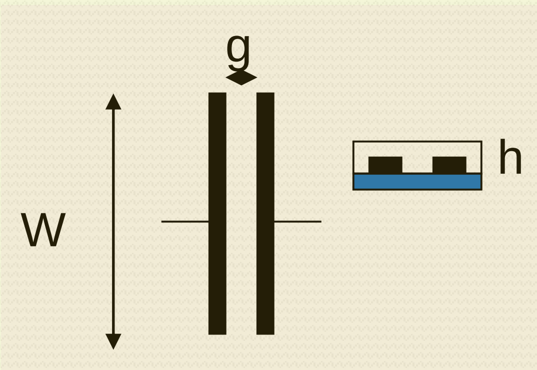
1. Water adsorption on SiO_2. (FTIR) About 7 monolayers of free water above 60% RH.

D.B. Asay and S.H. King, J. Phys. Chem. B. Vol 109, 35, 2005, 16761

2. Water is adsorbed at interfaces of thin hydrophilic or hydrophobic polymer films and SiO_2. Water layer thickness extends 2.5+/-1 nm into the film. (X-ray and Neutron reflectivity).
B.D. Vogt et al. Langmuir 2004, 20, 5285-5290.

3. Water is adsorbed on Ti and on Gold…

	No contact resistance	With contact resistance*
Analyte sensitivity	$r_a^f \equiv \dfrac{d\rho_f}{dC_a}$	$r_a^c \equiv \dfrac{d\rho_c}{dC_a}$



$$R = \frac{g\rho_f}{Wh}$$

$$R = \frac{g\rho_f}{Wh} + \frac{2\rho_c}{Wh}$$

$$\Delta R = \frac{g r_a^f}{Wh}\Delta C_a$$

$$\Delta R = \left(\frac{g r_a^f}{Wh} + \frac{2 r_a^c}{Wh}\right)\Delta C_a$$

Response

$$\frac{\Delta R}{R} = \frac{r_a^f}{\rho_f}\Delta C_a$$

Geometry independent

$$\frac{\Delta R}{R} = \left(\frac{g r_a^f + 2 r_a^c}{g\rho_f + 2\rho_c}\right)\Delta C_a$$

Gap dependent

For large contact-resistance sensitivity.

$$\frac{\Delta R}{R} = \frac{2 r_a^c}{g\rho_f + 2\rho_c}\Delta C_a$$

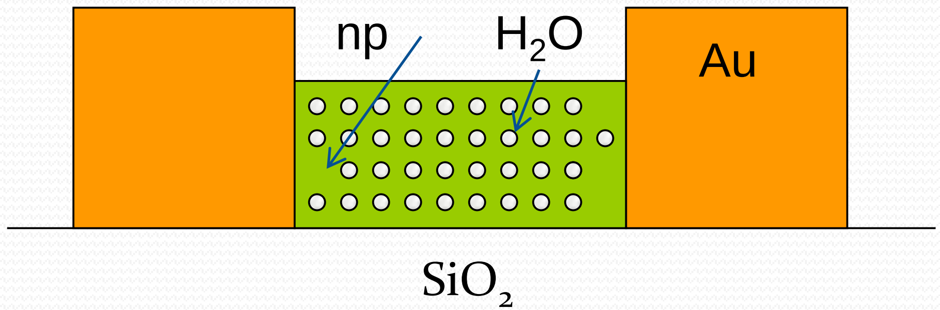
Gap dependent

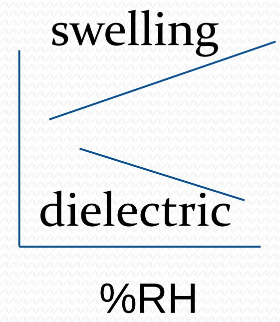
*(Adaptation of the model of Ancona et al. IEEE Sensor Journal. 2006, 6, 1405-.)

Where can the water be adsorbed and what are the implications?

Adsorption in NP

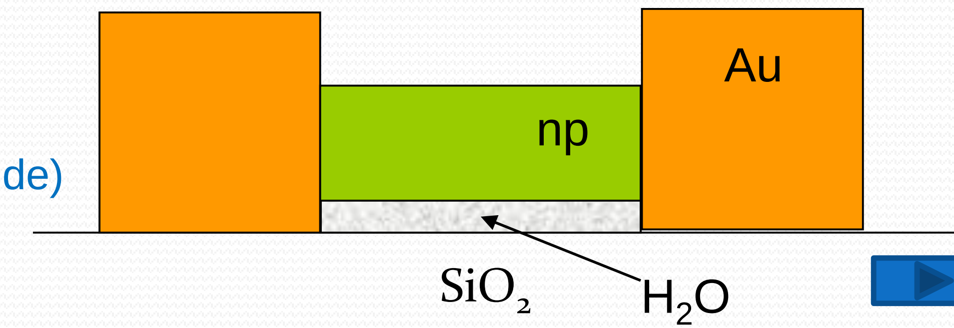
Intrinsic response
Gap independent

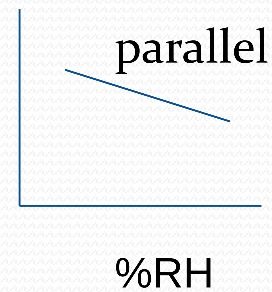




Adsorption on SiO2

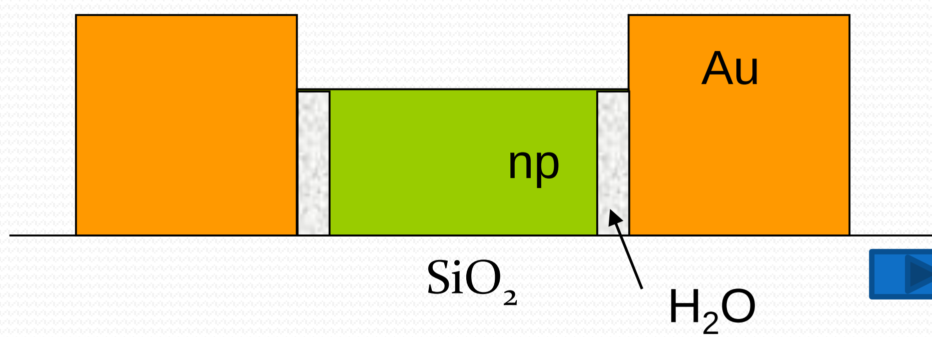
Parallel conduction
Path (ionic contamination needed to explain magnitude)
Gap independent

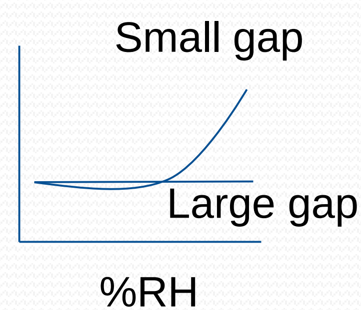




Adsorption on electrodes

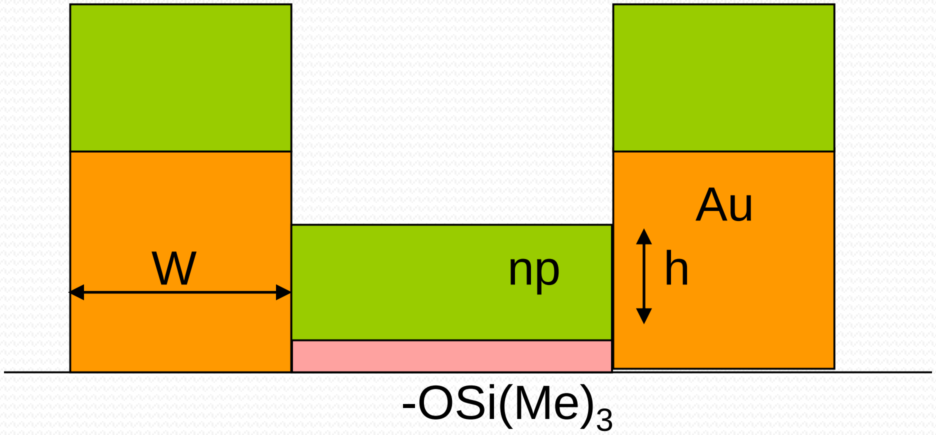
Contact resistance
Series resistance
Gap dependent



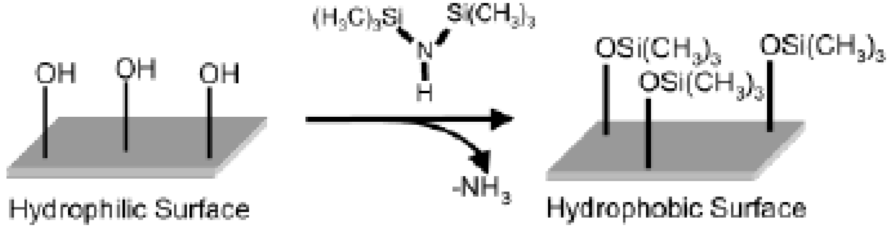


HMDS treatment

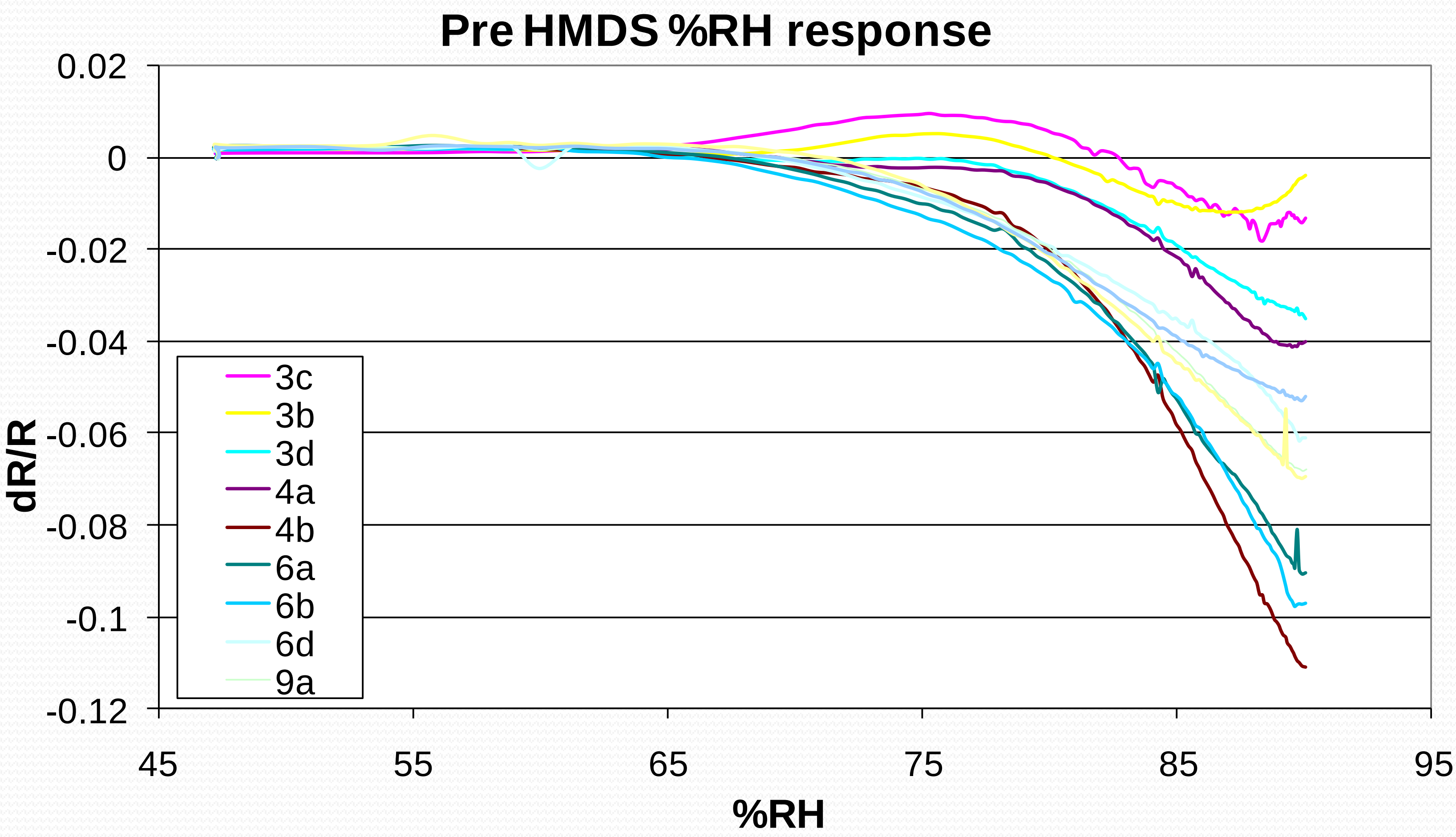
- Pre-jetting.
- Post jetting.
- Vapor phase
- Flooding.

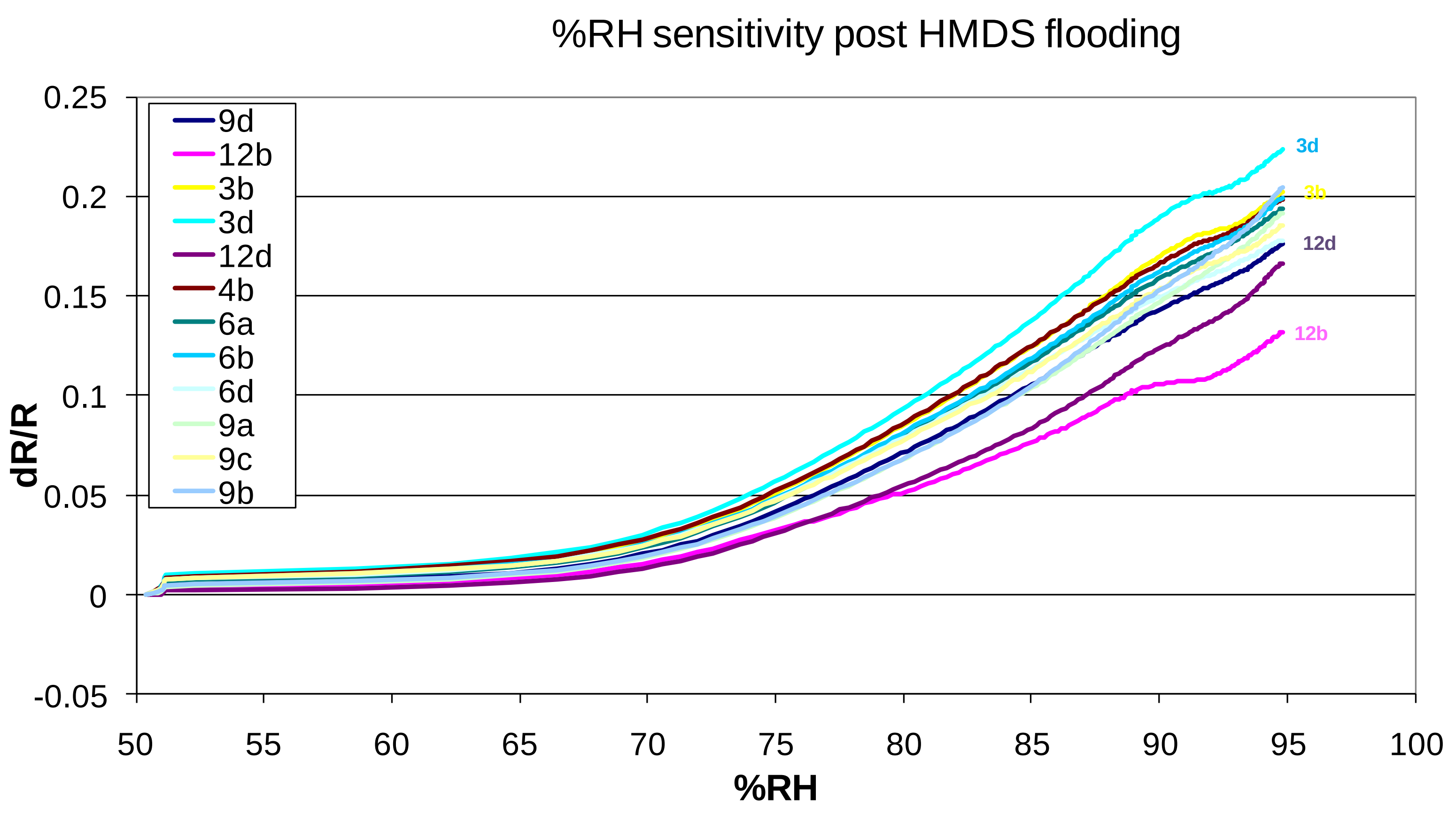


Scheme 1



~~Parallel conduction path~~


Pre HMDS %RH response
dR/R
%RH
0.02
0
-0.02
-0.04
-0.06
-0.08
-0.1
-0.12
45
55
65
75
85
95
3c
3b
3d
4a
4b
6a
6b
6d
9a

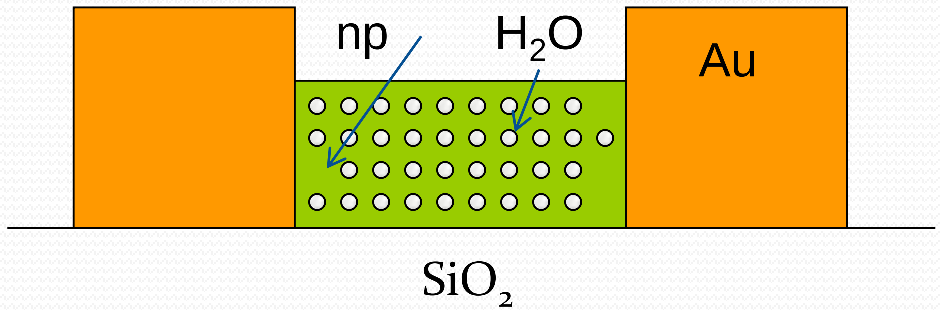


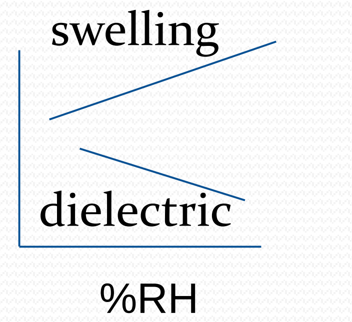
HMDS flooding caused a shift in the direction of the response.
The response is intrinsic and contact resistance related.

Where can the water be adsorbed and what are the implications?

Adsorption in NP

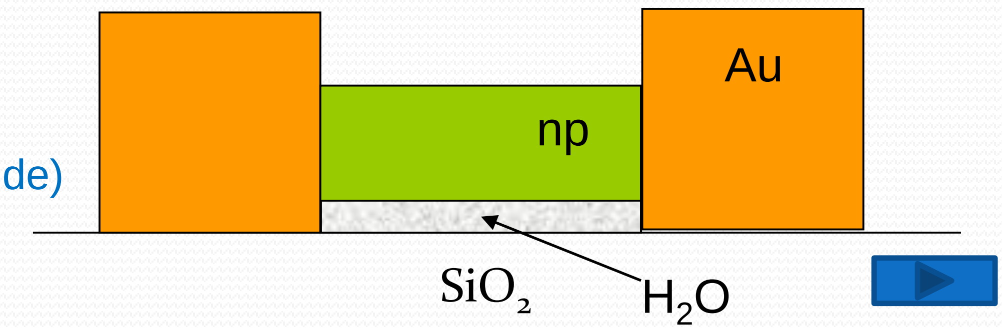
Intrinsic response
Gap independent

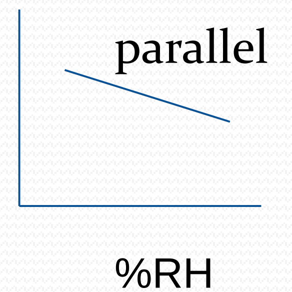




Adsorption on SiO2

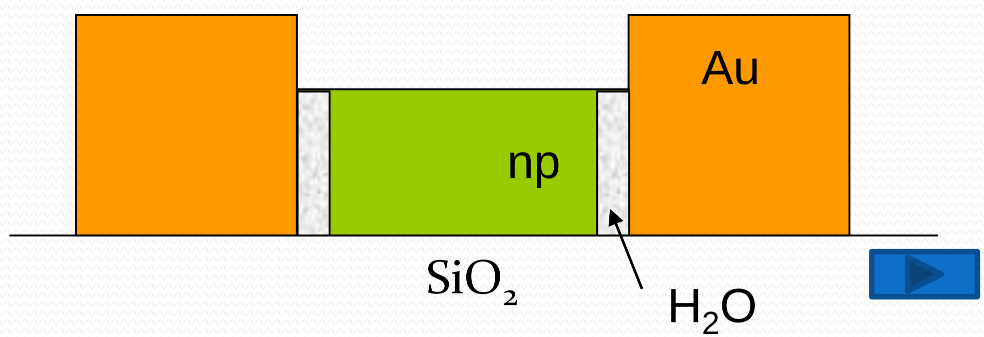
Parallel conduction
Path (ionic contamination needed to explain magnitude)
Gap independent

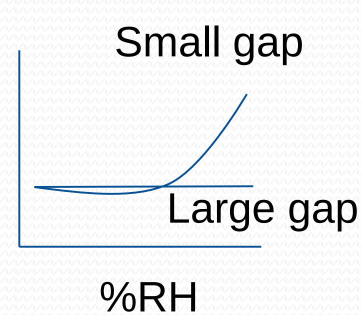


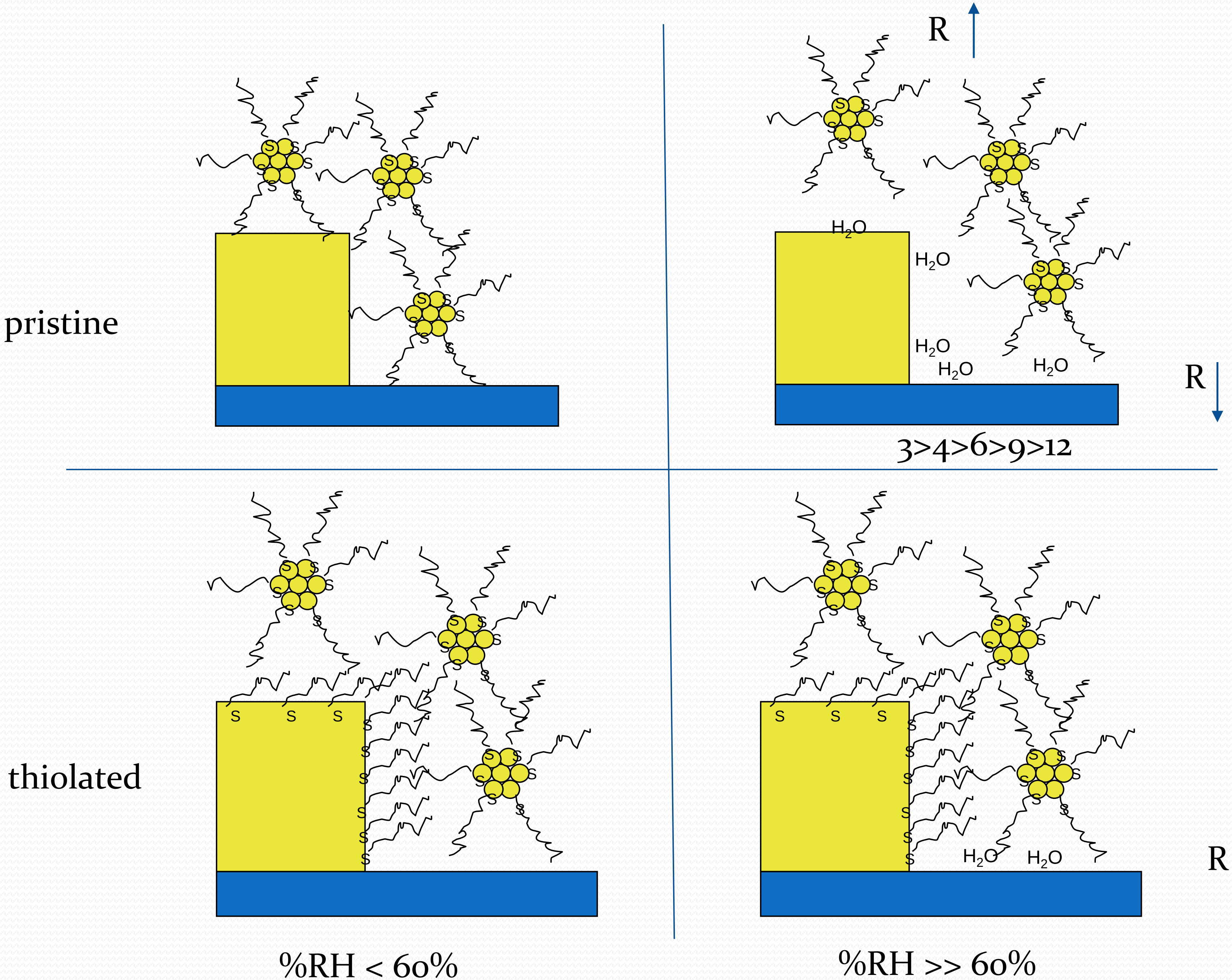


Adsorption on electrodes

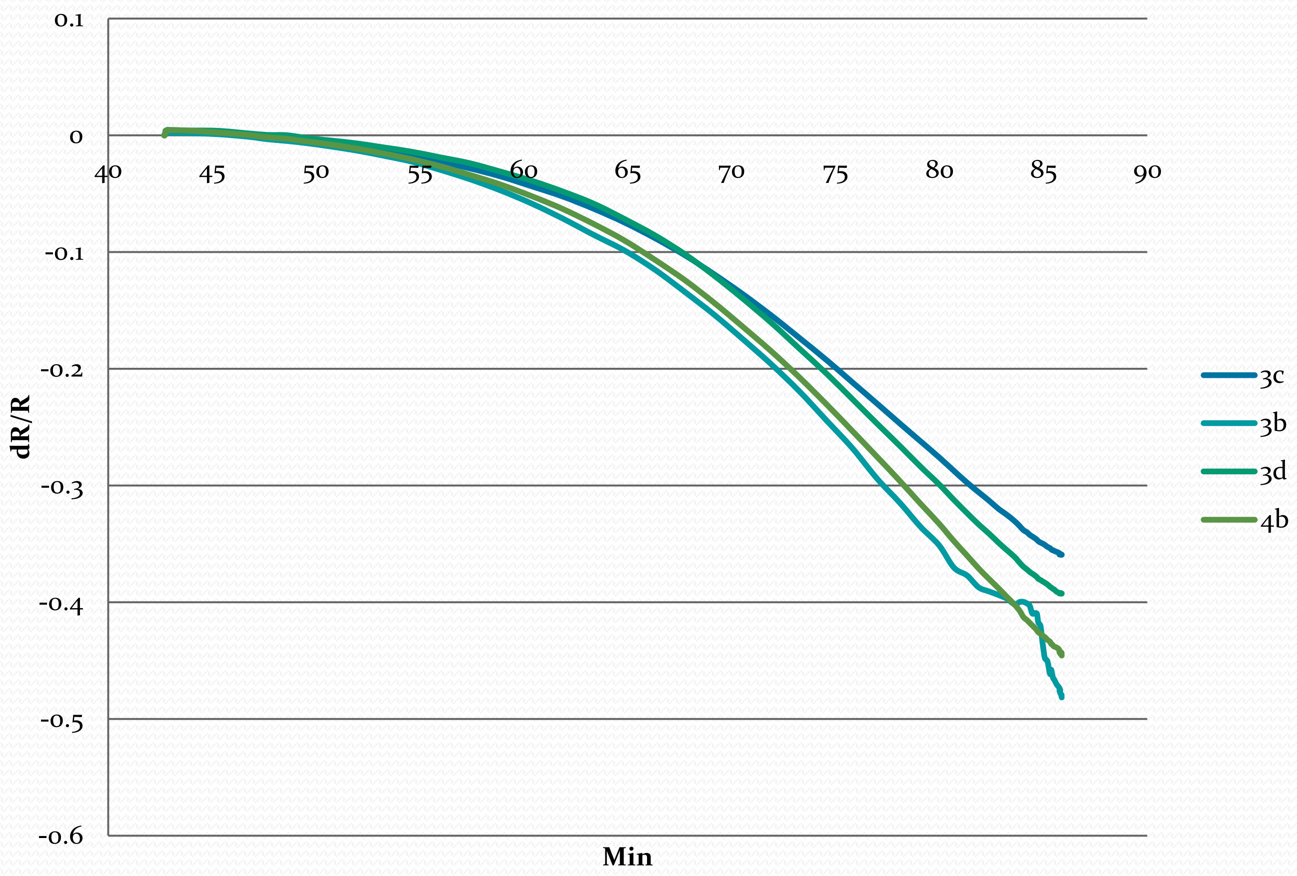
Contact resistance
Series resistance
Gap dependent





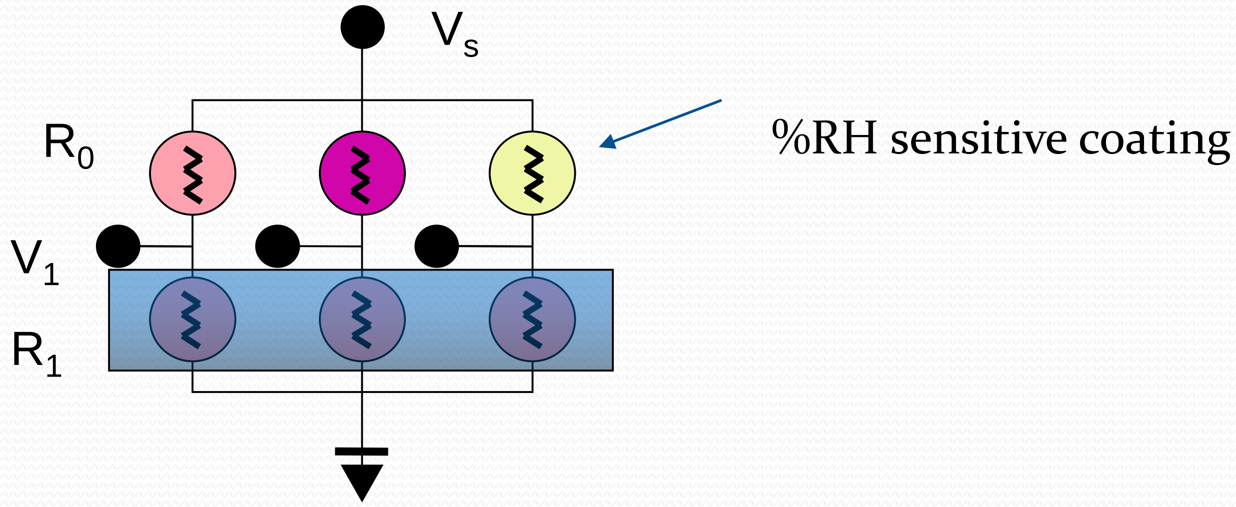

pristine
thiolated
R
R
R
H_2O
3>4>6>9>12
S
%RH < 60%
%RH >> 60%

Response to %RH of C8SH treated transducers (24x1 drops)

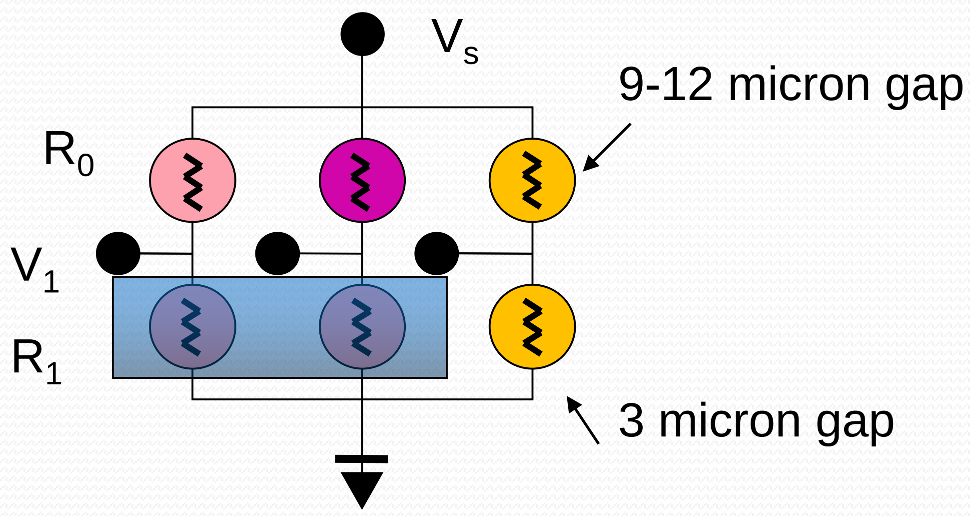


A possible implementation of the gap dependence of the humidity response in a humidity sensor that is insensitive to solvents.

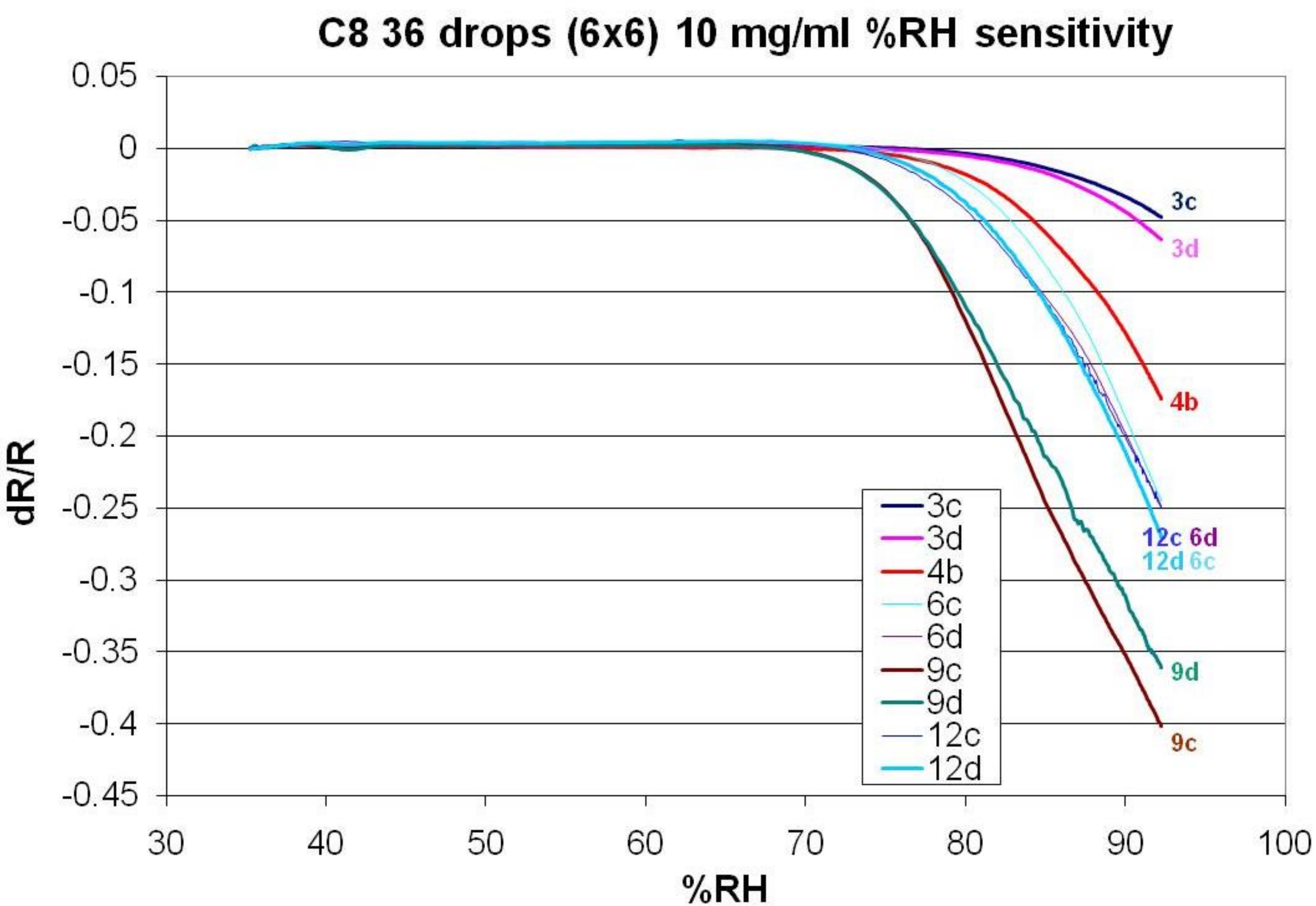
Array option



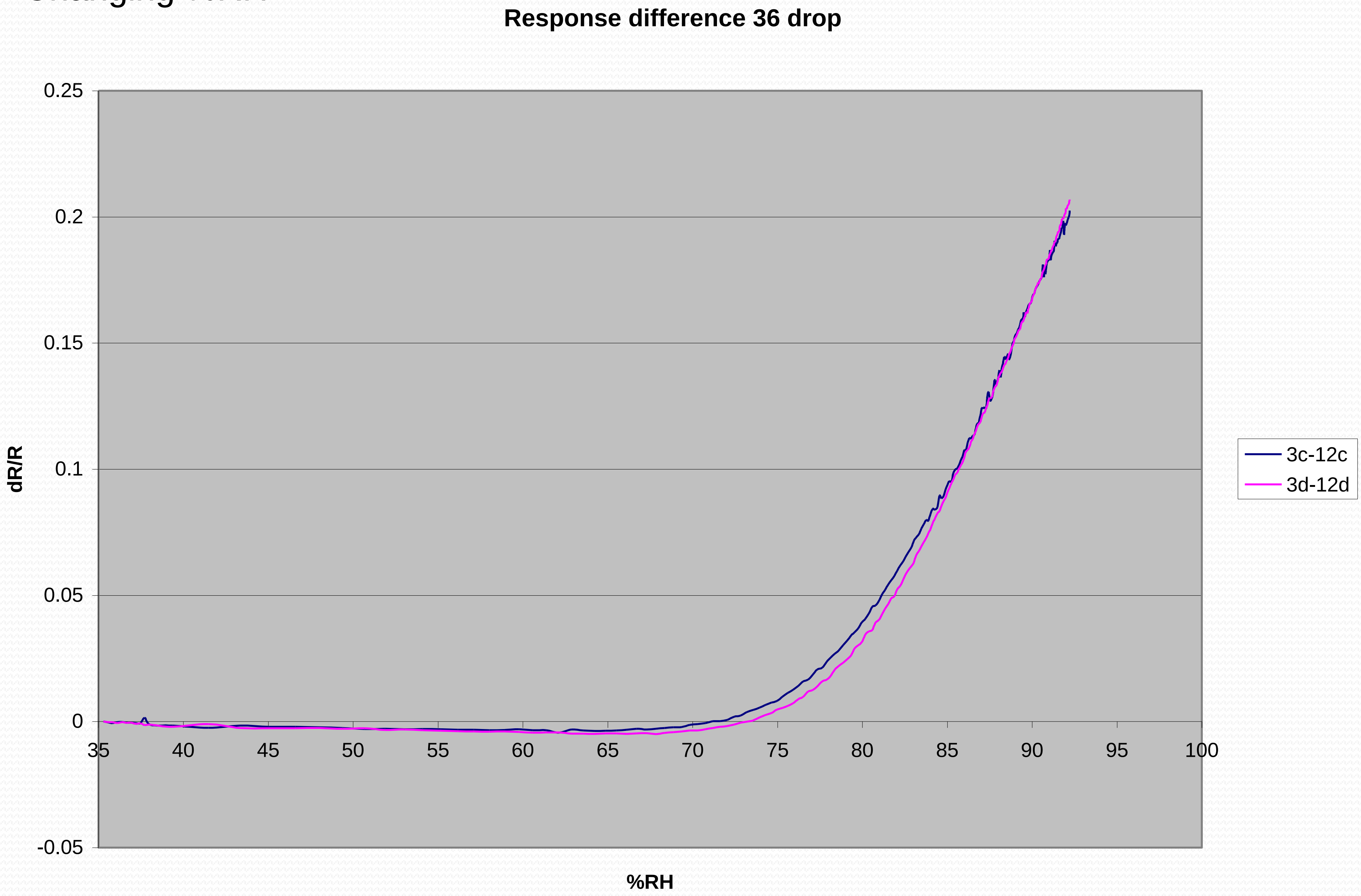
proposed



We can use the gap scaling effect to create a humidity sensor that is insensitive to solvents.



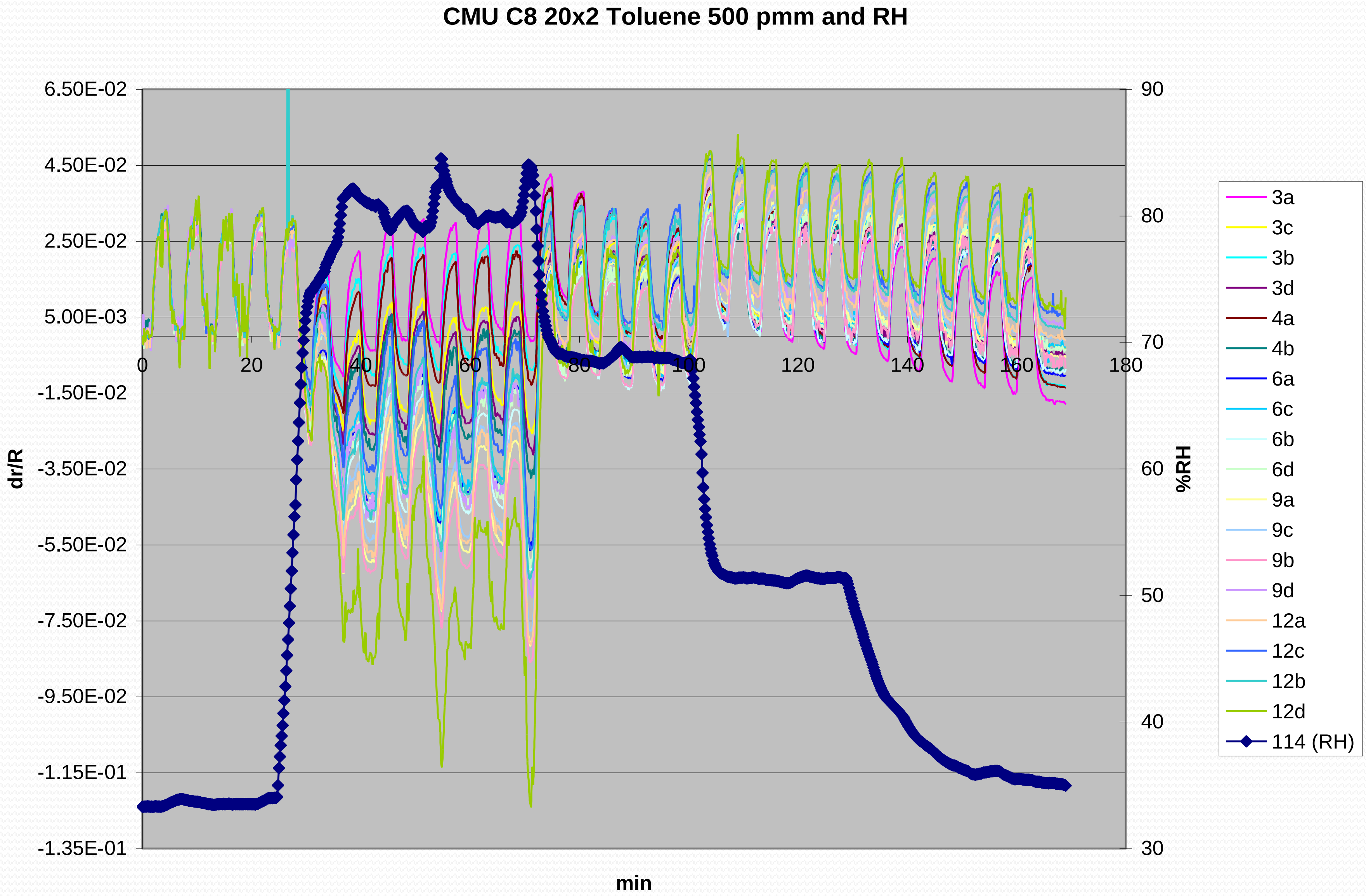
Changing %RH

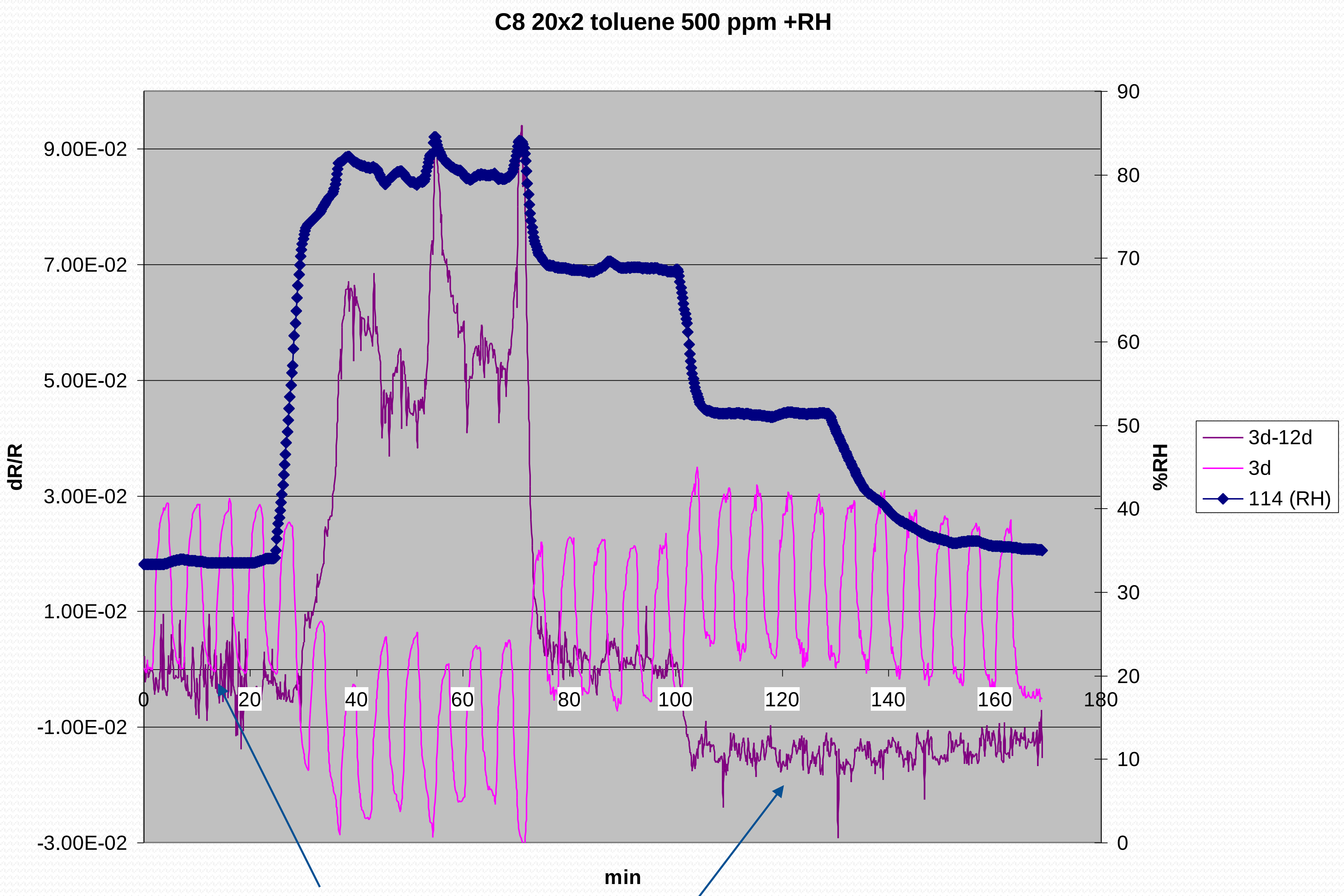


Response difference 36 drop
0.25
0.2
0.15
0.1
0.05
0
-0.05
dR/R
35
40
45
50
55
60
65
70
75
80
85
90
95
100
%RH
3c-12c
3d-12d

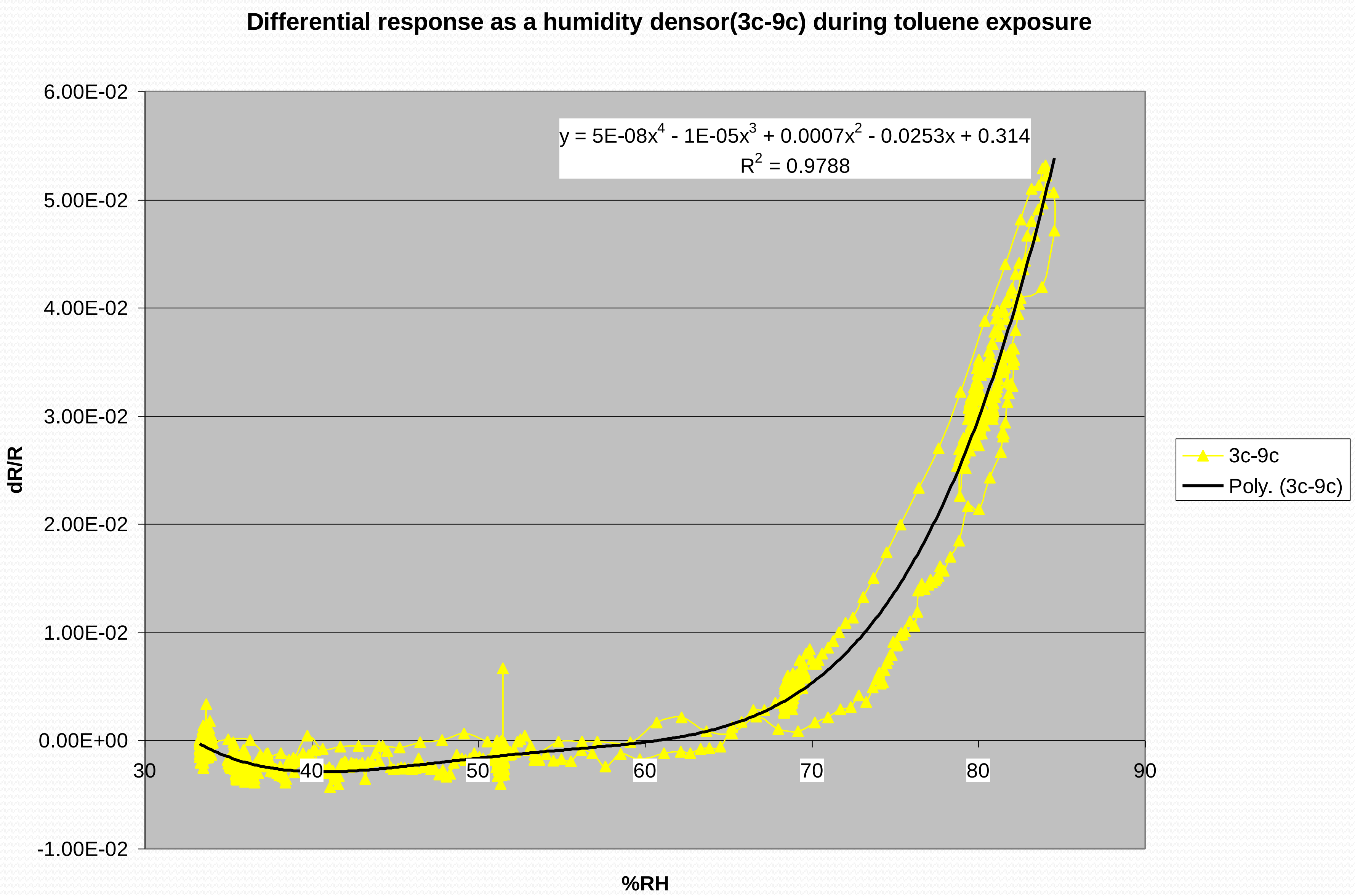
Toluene pulsing experiment while changing humidity.

.

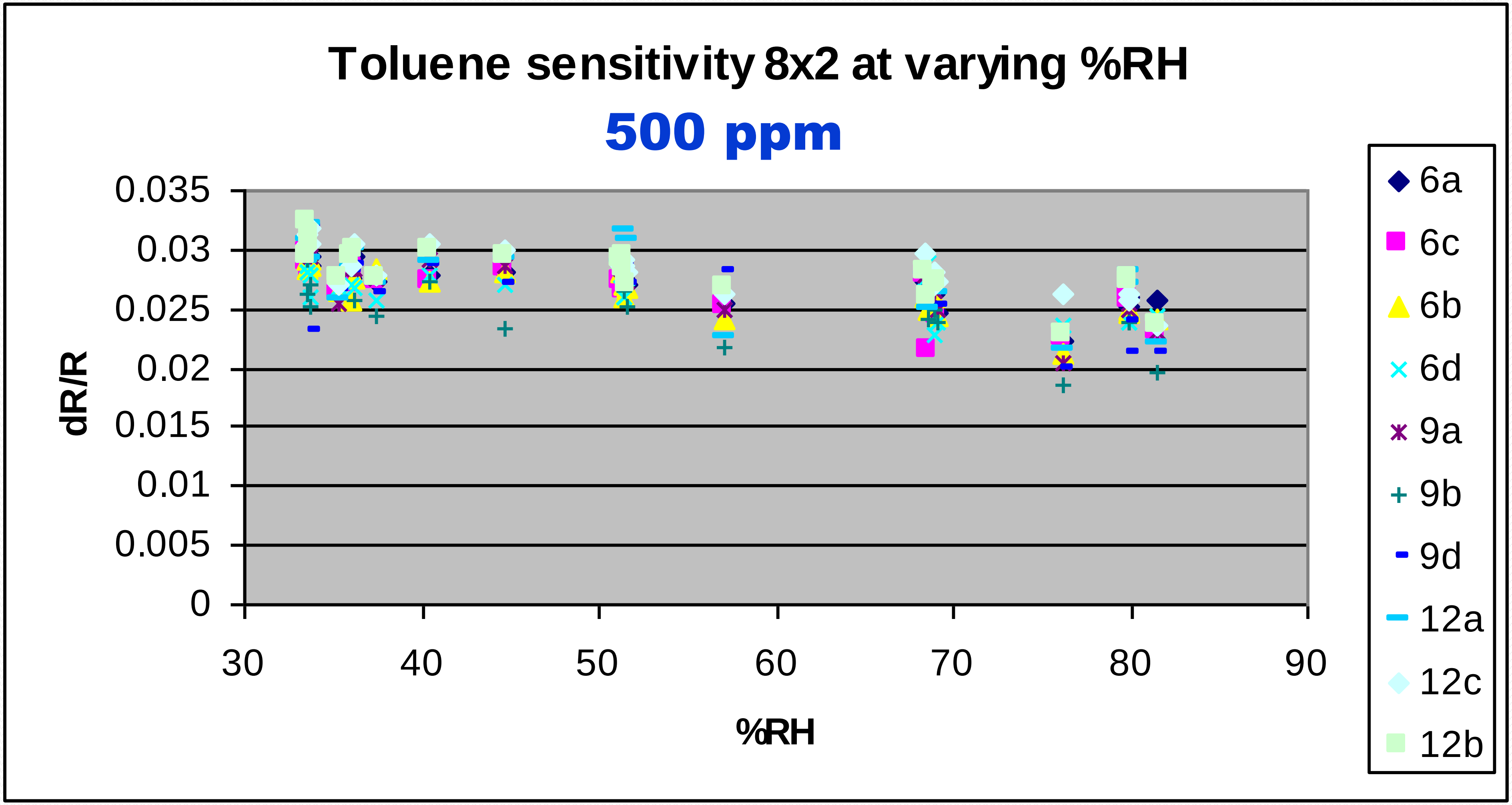




The response to %RH is not affected by toluene!!!

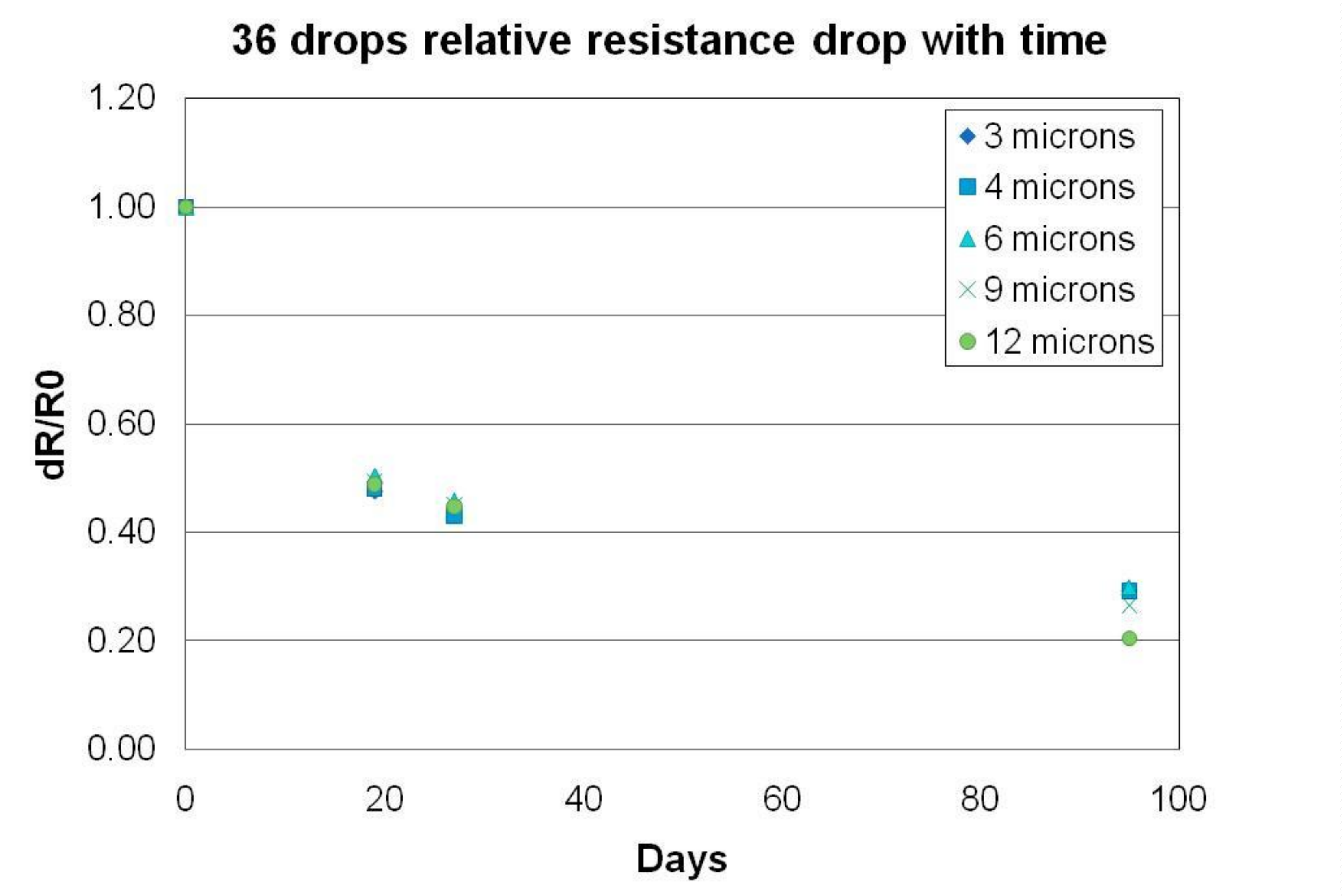


Differential response as a humidity densor(3c-9c) during toluene exposure
y = 5E-08x4 - 1E-05x3 + 0.0007x2 - 0.0253x + 0.314
R2 = 0.9788
6.00E-02
5.00E-02
4.00E-02
3.00E-02
2.00E-02
1.00E-02
0.00E+00
-1.00E-02
30
40
50
60
70
80
90
dR/R
%RH
3c-9c
Poly. (3c-9c)

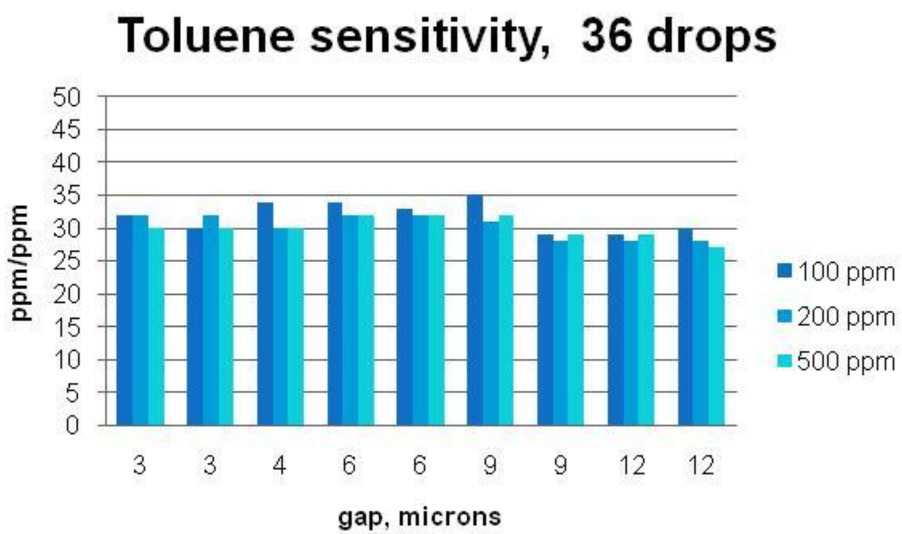


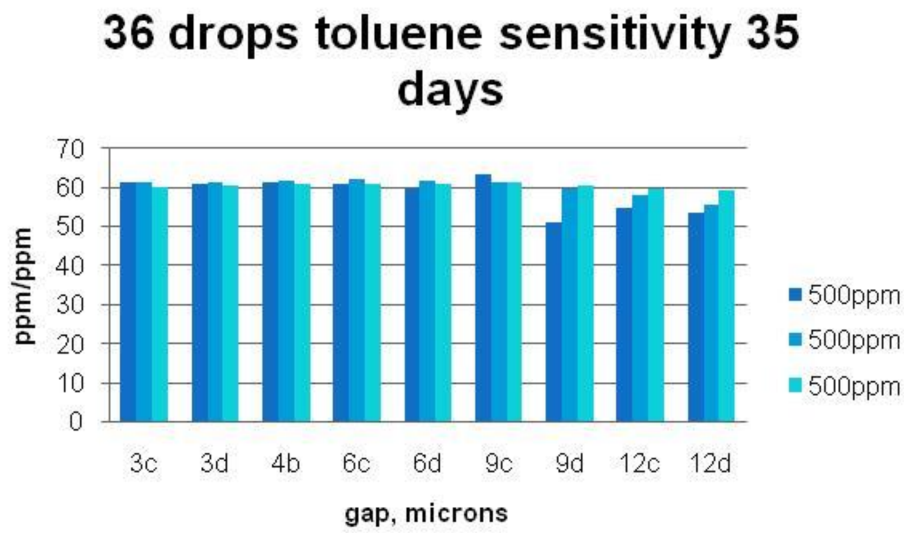
Toluene sensitivity 8x2 at varying %RH
500 ppm
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
dR/R
30
40
50
60
70
80
90
%RH
6a
6c
6b
6d
9a
9b
9d
12a
12c
12b

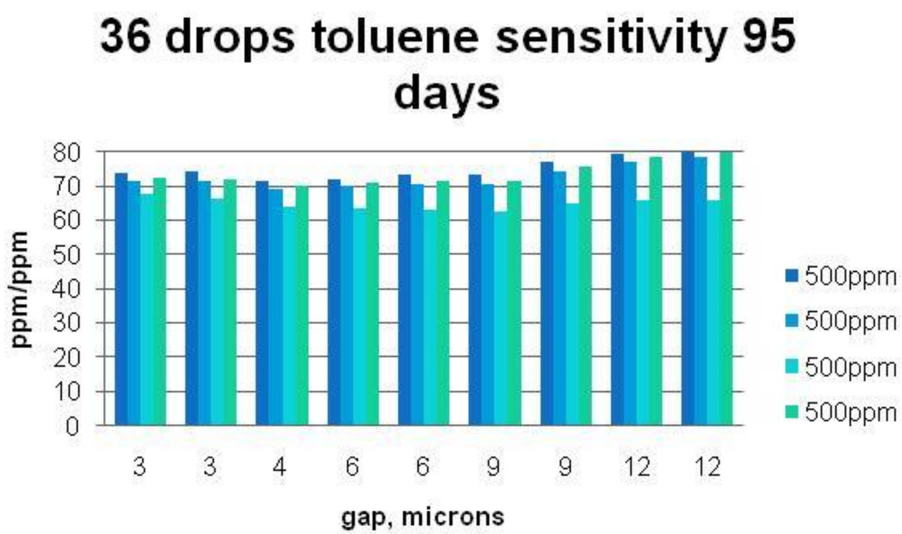
Aging

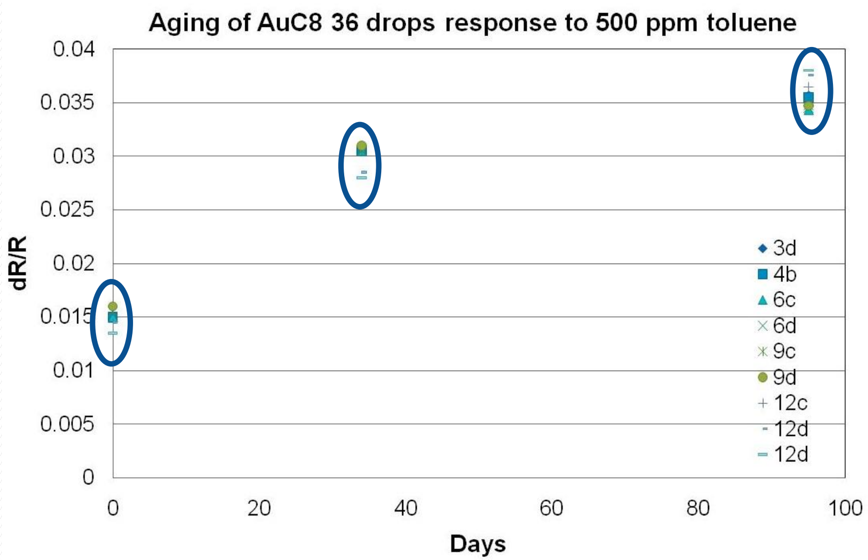


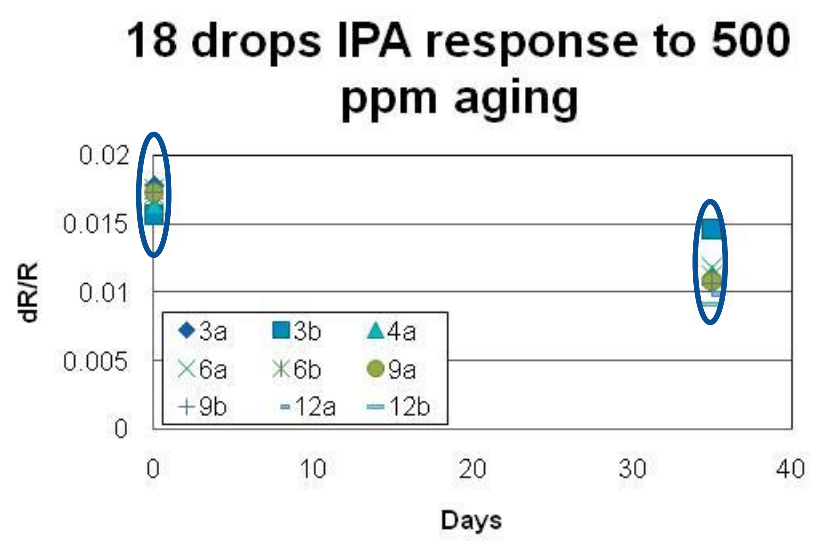
36 drops relative resistance drop with time
1.20
1.00
0.80
0.60
0.40
0.20
0.00
dR/R0
0
20
40
60
80
100
Days
3 microns
4 microns
6 microns
9 microns
12 microns

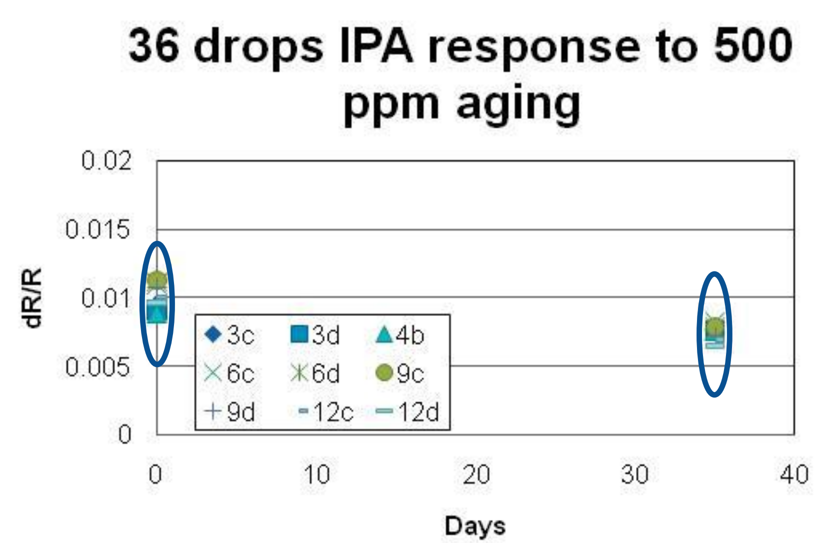

Toluene sensitivity, 36 drops
ppm/ppm
gap, microns
100 ppm
200 ppm
500 ppm


36 drops toluene sensitivity 35 days
ppm/ppm
gap, microns
500ppm
500ppm
500ppm

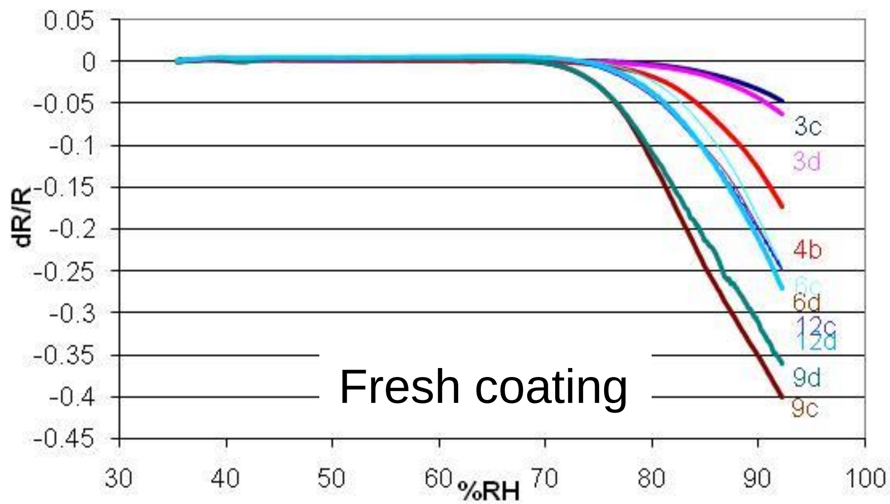

36 drops toluene sensitivity 95 days
ppm/ppm
gap, microns
500ppm
500ppm
500ppm
500ppm

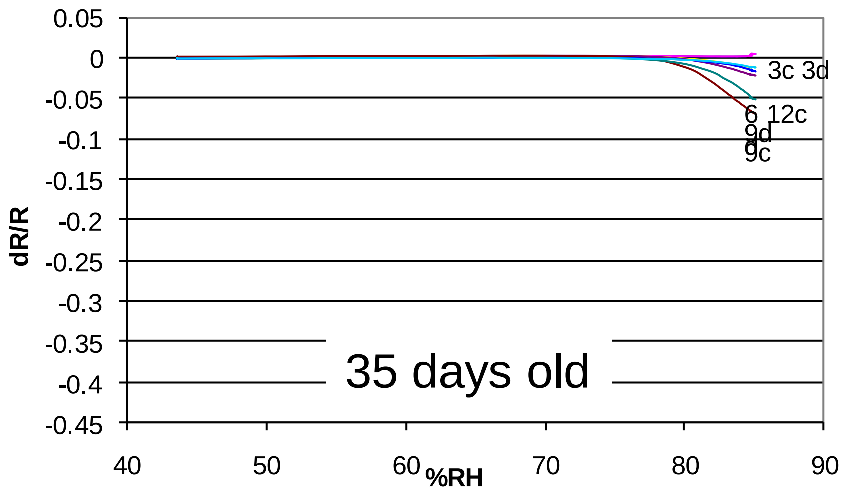

Aging of AuC8 36 drops response to 500 ppm toluene
dR/R
Days
3d
4b
6c
6d
9c
9d
12c
12d
12d

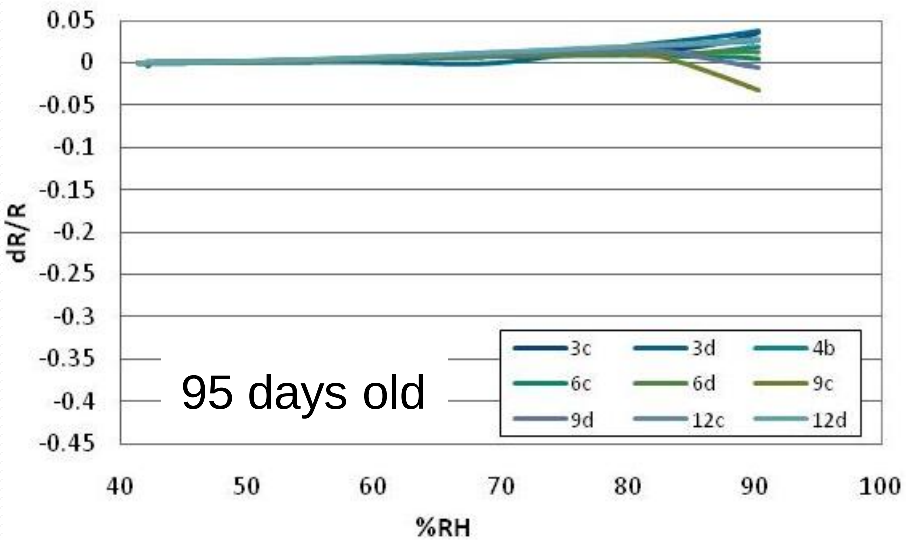

18 drops IPA response to 500 ppm aging
dR/R
0.02
0.015
0.01
0.005
0
0
10
20
30
40
Days
3a
3b
4a
6a
6b
9a
9b
12a
12b


36 drops IPA response to 500 ppm aging
dR/R
0.02
0.015
0.01
0.005
0
0
10
20
30
40
Days
3c
3d
4b
6c
6d
9c
9d
12c
12d

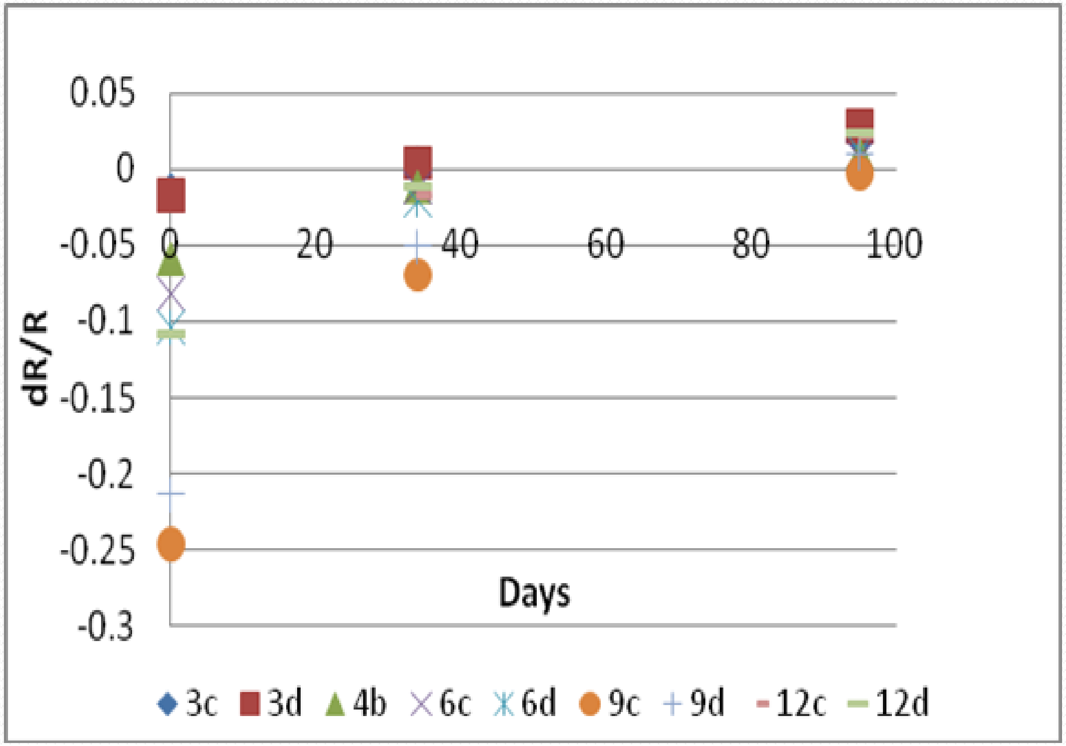
Sensitivity to %RH - CMU C8 36 drops





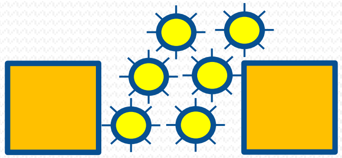


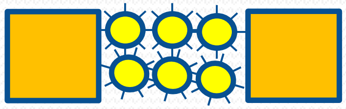
Aging of the response to 85% RH of the 36 drops transducers (3c, 3d = 3 micron gaps, etc.).



Aging

- Increase in conductivity.
- Increase in sensitivity to toluene.
- Slight decrease in sensitivity to 2-propanol.
- Decrease in sensitivity to humidity along with decrease in gap width effect.





Possible explanation

- Better packing (annealing).
- Better shielding of both the SiO_2 and the electrodes.

Alternative explanation

- Monolayer degradation.
- Physical contact between the NP themselves and between them and the electrodes. Explains resistance drop but not increase in sensitivity to toluene.
- Liberated thiol and/or disulfide adhere to the electrodes. Should eliminate gap width dependence but increase contact resistance. Does not explain reduced water adsorption on the SiO2.

Summary

- An inkjetted chemisensor array for ESLI was demonstrated.
- Advantages of inkjetting for chemisensor arrays were discussed.
- A parametric study revealed an unreported gap-width dependence sensitivity to %RH at %RH > 60% which diminished upon aging.
- A novel humidity sensor with no solvent cross-selectivity was demonstrated. Its implementation relies on the ability to stabilize interfaces.
- %RH response can be tailored by surface treatment.
- Testing of other chemiresistive coatings is continuing.
- Incorporation of other technologies (e.g. chemicapacitors) is underway.

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