Óbuda University

Doctoral School on Materials Science and Technologies

6th semester's progress presentation

{Calixresorcinarenes ionophores: a heavy metals ions detection application}

By: Larbi Eddaif

Supervisor: Dr. Shaban Abdul

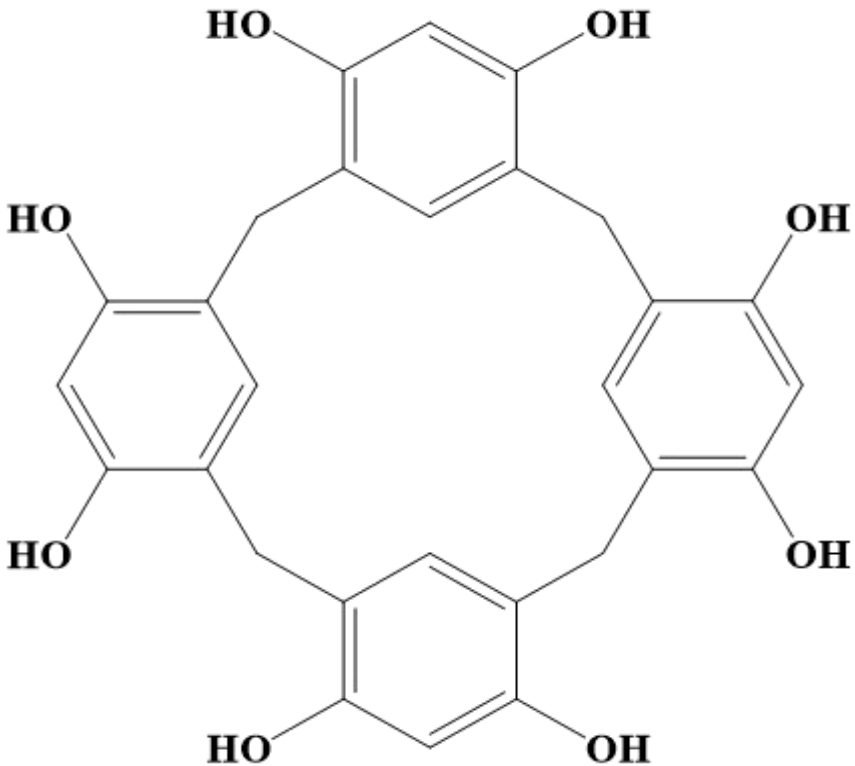
Budapest, January 23rd 2019

Outlines

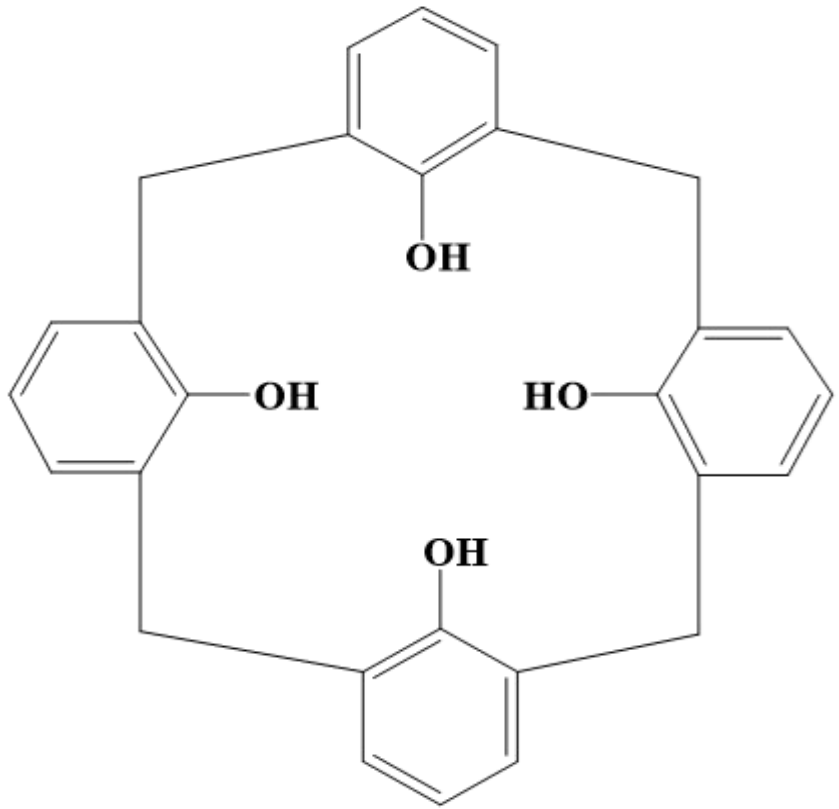
Thesis Topic

"Calixresorcinarenes/calixarenes ionophores for the HM cations monitoring in water environment"

Molecular structures of Calix[4]resorcinarene and Calix[4]arene



Calix[4]resorcinarene



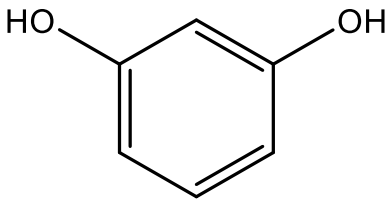
Calix[4]arene

Accomplished Work

Their synthesis is based on the condensation between para-substituted phenols/resorcinols and aldehydes

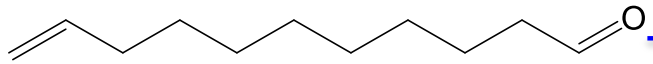
- **A**: C-dec-9-en-1-ylcalix[4]resorcinarene
- **A'**: C-trans-2, cis-6-octa-1,5-dien-1-ylcalix[4]resorcinarene,
- **B**: C-dec-9-enylcalix[4]resorcinarene-O-(S-)-α-methylbenzylamine
- **C**: C-dec-9-enylcalix [4]resorcinarene-O-(R+)-α-methylbenzylamine
- **D**: C-nonylcalix[4]resorcinarene,
- **E**: Tert-butylcalix[4]arene,
- **F**: C-undecylcalix[4]resorcinarene.

Synthetic approach of compound A



Resorcinol

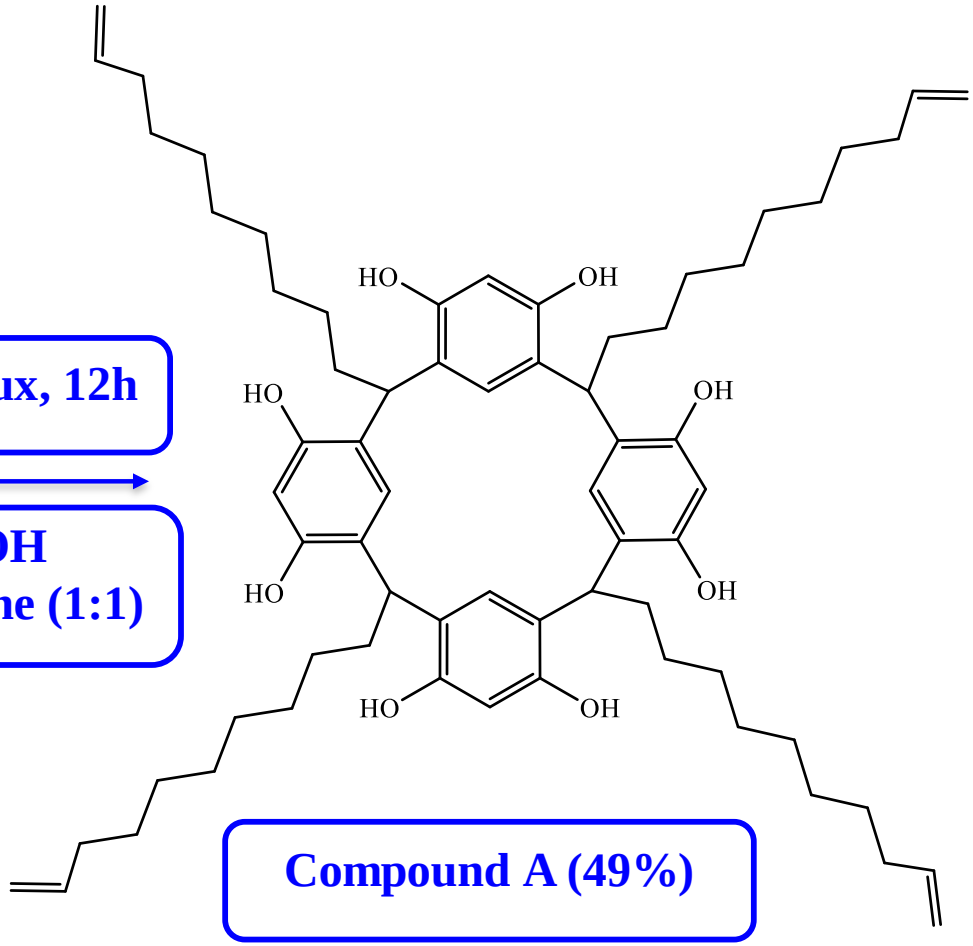
+



Undec-10-en-1-yl aldehyde

HCl/ Reflux, 12h

MeOH
Ac:Hexane (1:1)



Compound A (49%)

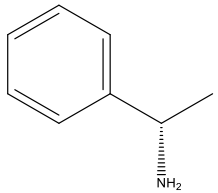
Eddaif, L., et al. J Therm Anal Calorim (2019) https://doi.org/10.1007/s10973-018-7978-0

Synthetic route of compounds B and C.

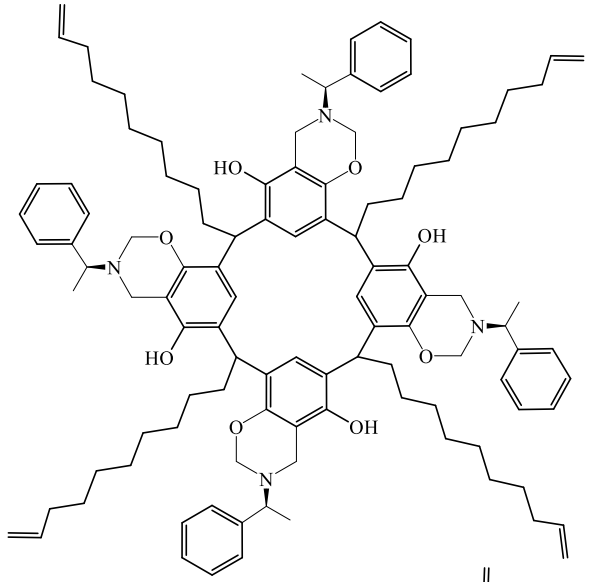
Compound A

THF: MeOH (1:1)
Paraformaldehyde

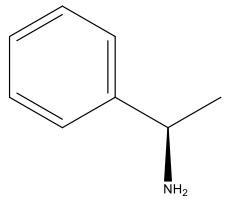
Stirring (Ar, 1h)
Reflux, 12h/ ACN



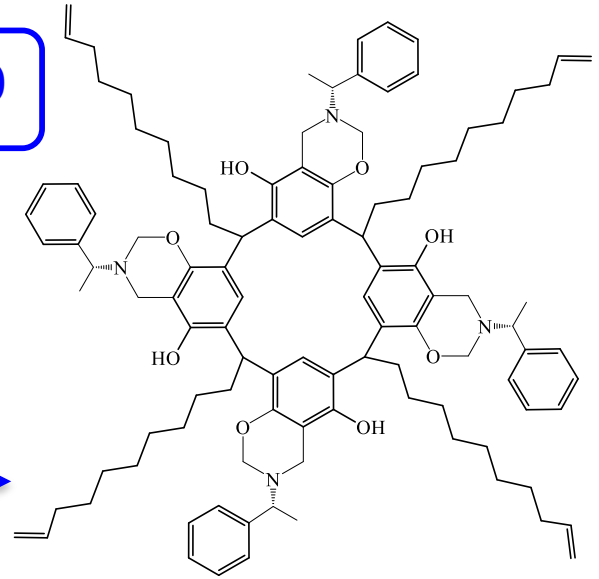
S-(-)-α-methylbenzylamine



Compound B (50%)



R-(+)-α-methylbenzylamine



Compound C (50%)

Eddaif, L., et al. Arabian Journal of Chemistry (2019) https://doi.org/10.1016/j.arabjc.2019.09.002

Ionophores characterization

FTIR :

Functional groups determination;

^{1}H and ^{13}C NMR:

Proposed structures' validation;

TG-DSC-MS:

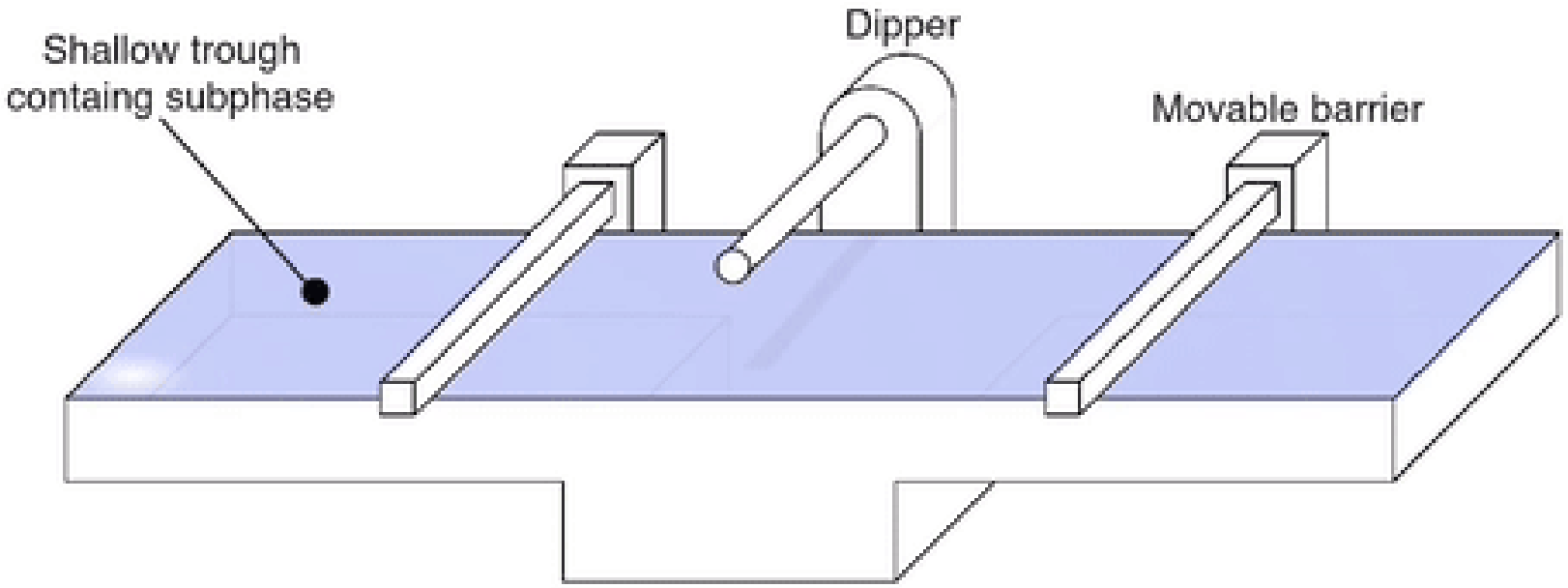
Molecules purity & thermal behavior;

XRD:

Crystallinity degree evaluation.

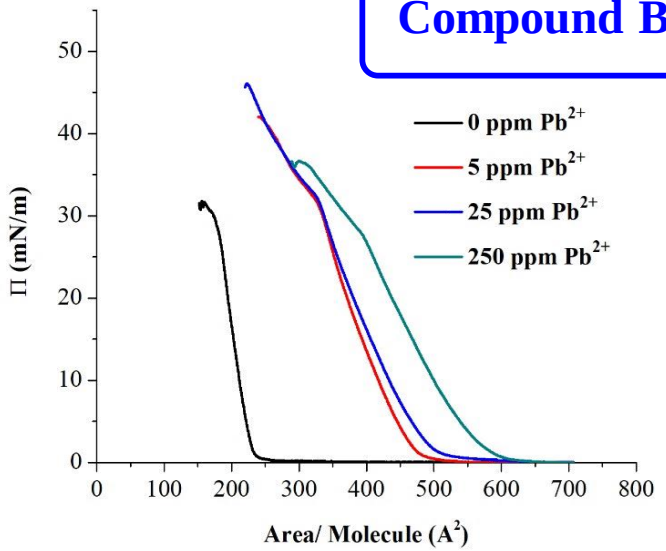
Main Findings

Langmuir Π-A Isotherms principle



Main Findings

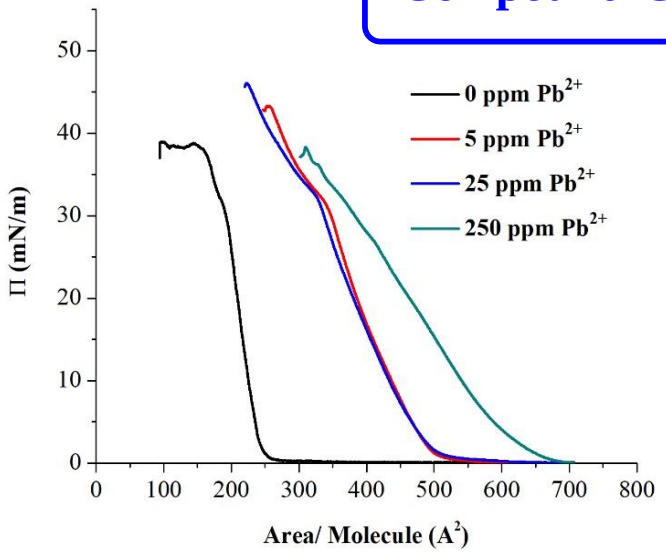
Compound B



Langmuir isotherms data for Compound B

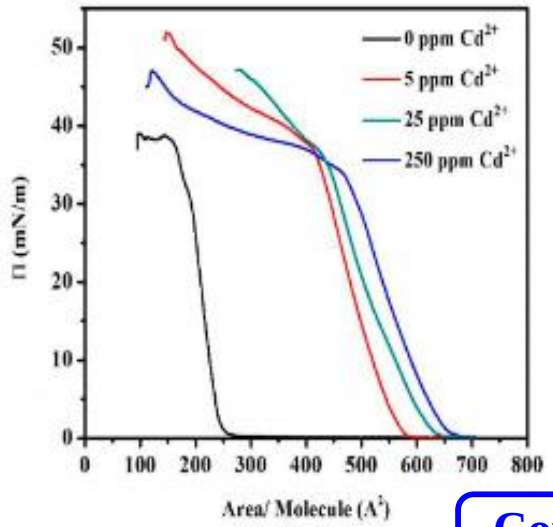
Studied HM	Concentration (ppm)	P_c (mN/m)	A_c (Å²/molecule)	A_{lim} (Å²/molecule)
Pb^{2+}	0 (Pure water)	39	100	240
	5	43	270	450
	25	46	235	490
	250	38	320	620

Compound C

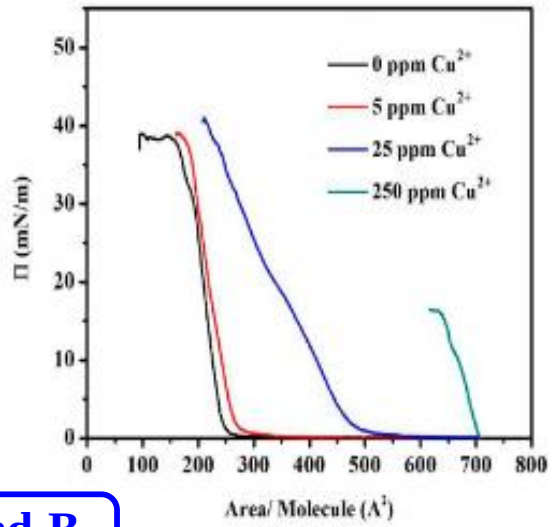


Langmuir isotherms data for Compound C

Studied HM	Concentration (ppm)	P_c (mN/m)	A_c (Å²/molecule)	A_{lim} (Å²/molecule)
Pb^{2+}	0 (Pure water)	32	170	230
	5	42	250	450
	25	46	230	480
	250	37	315	560

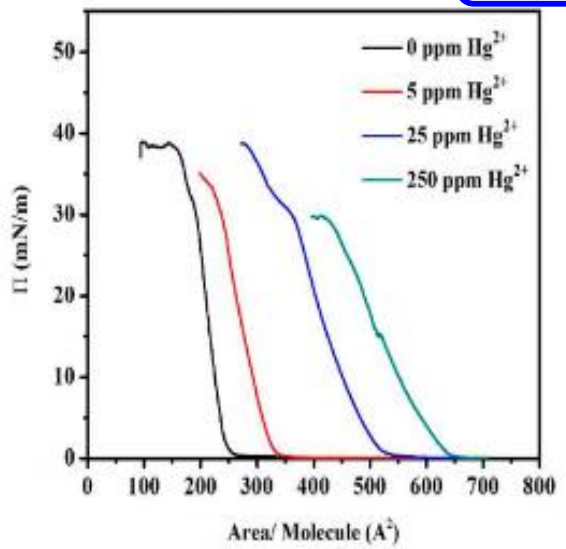


a



b

Compound B



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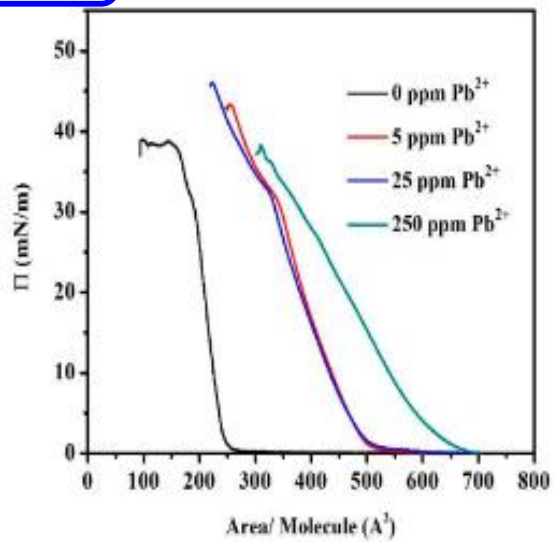

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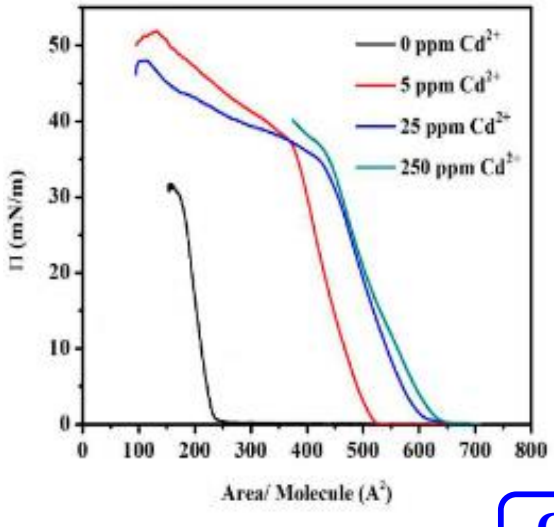
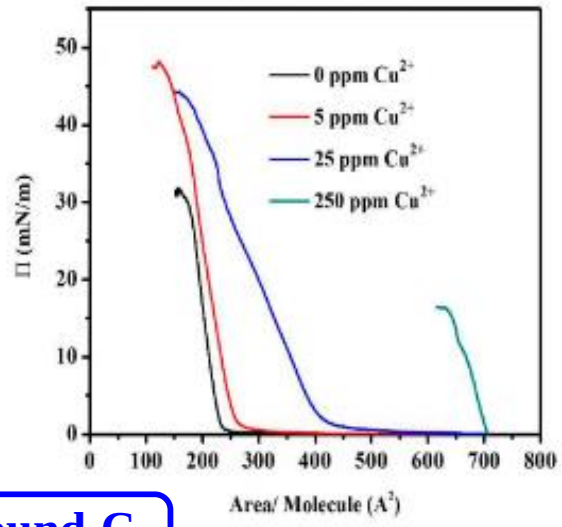


a

Compound C



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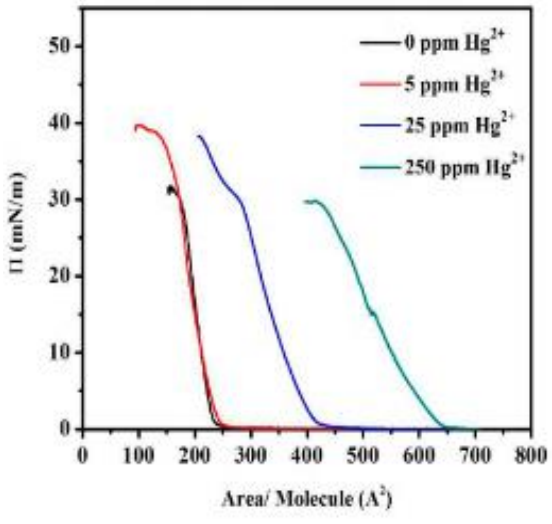

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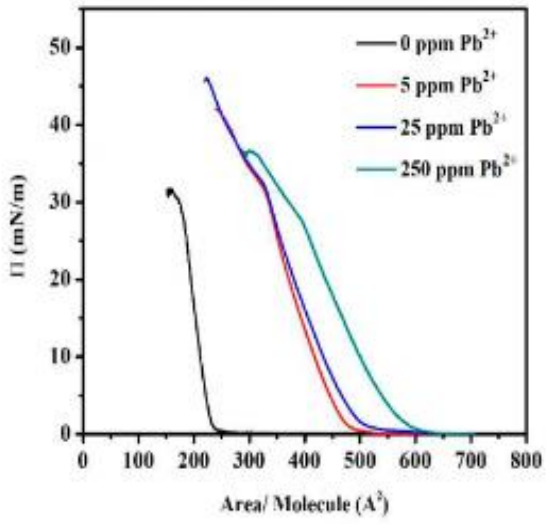
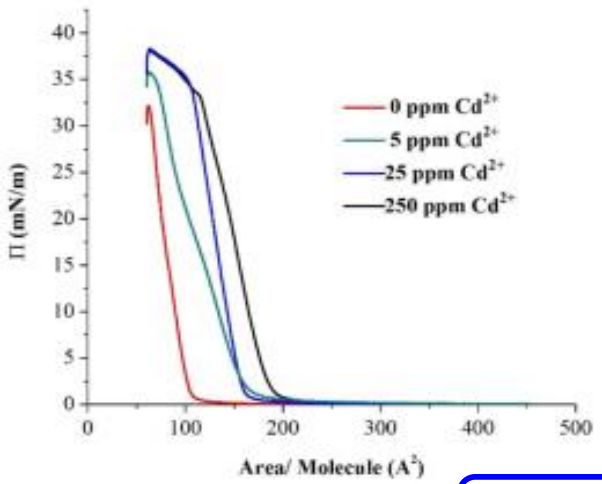
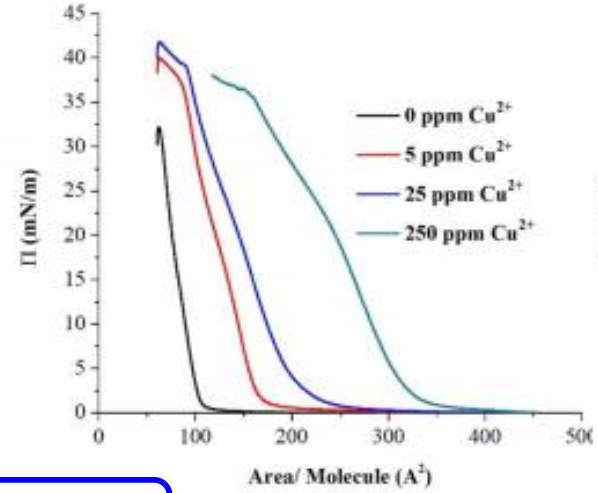


d

Eddaif, L., et al. Electroanalysis (2019), doi: 10.1002/elan.201900651

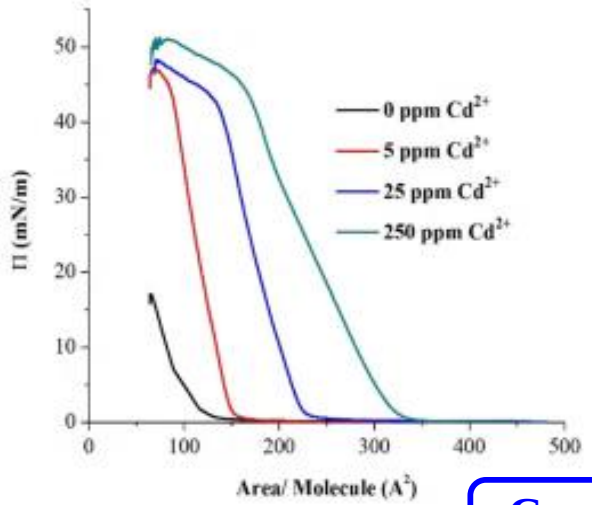


a



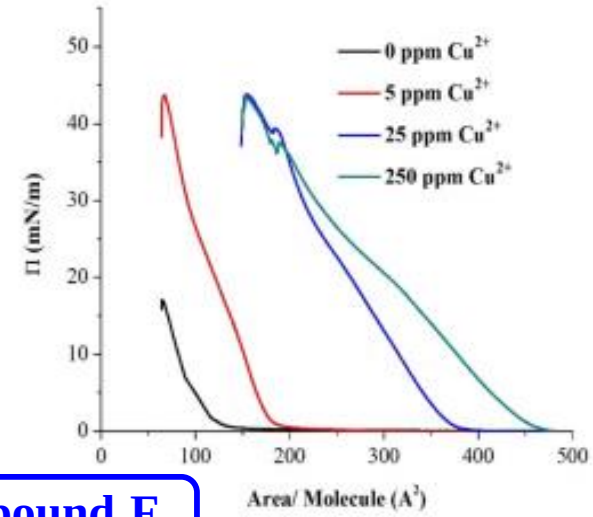
b

Compound A



a

Compound F



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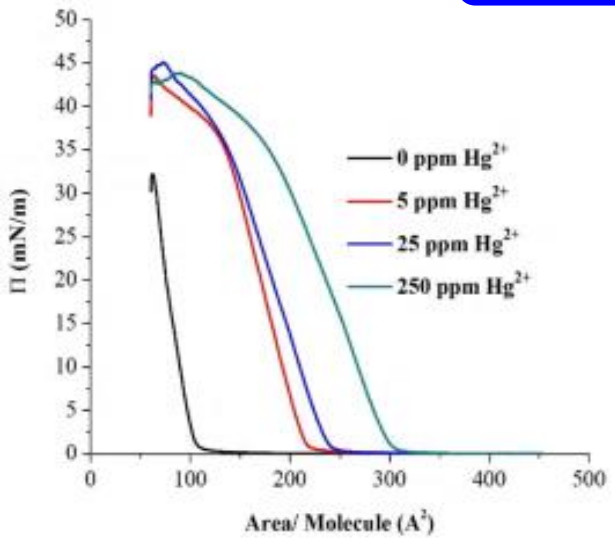

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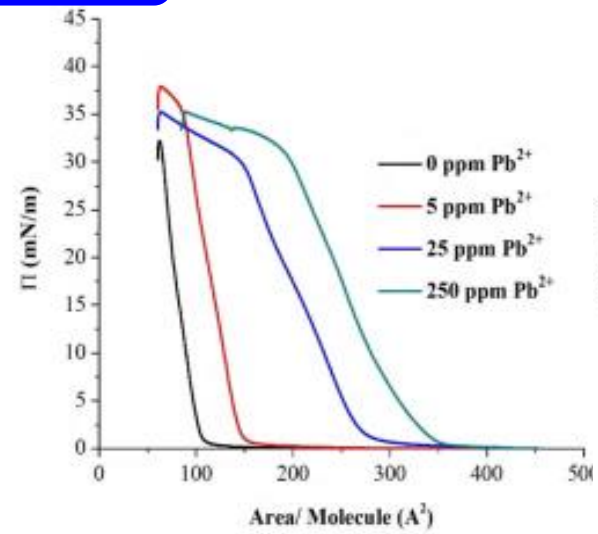

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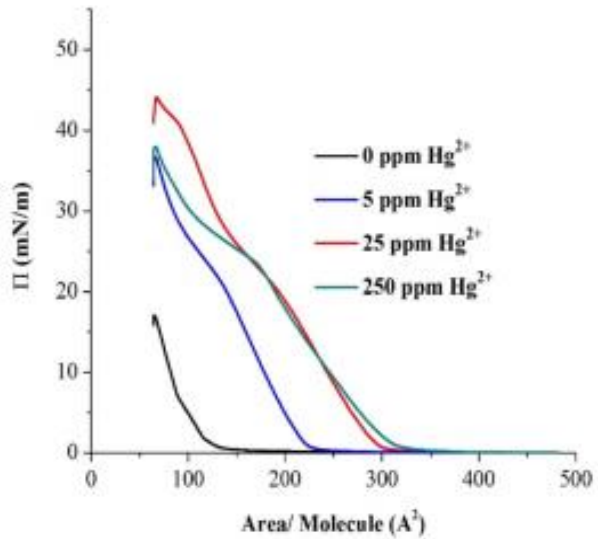

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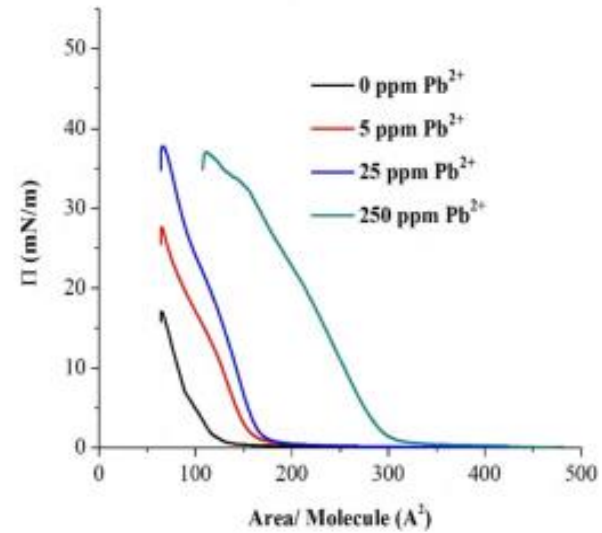


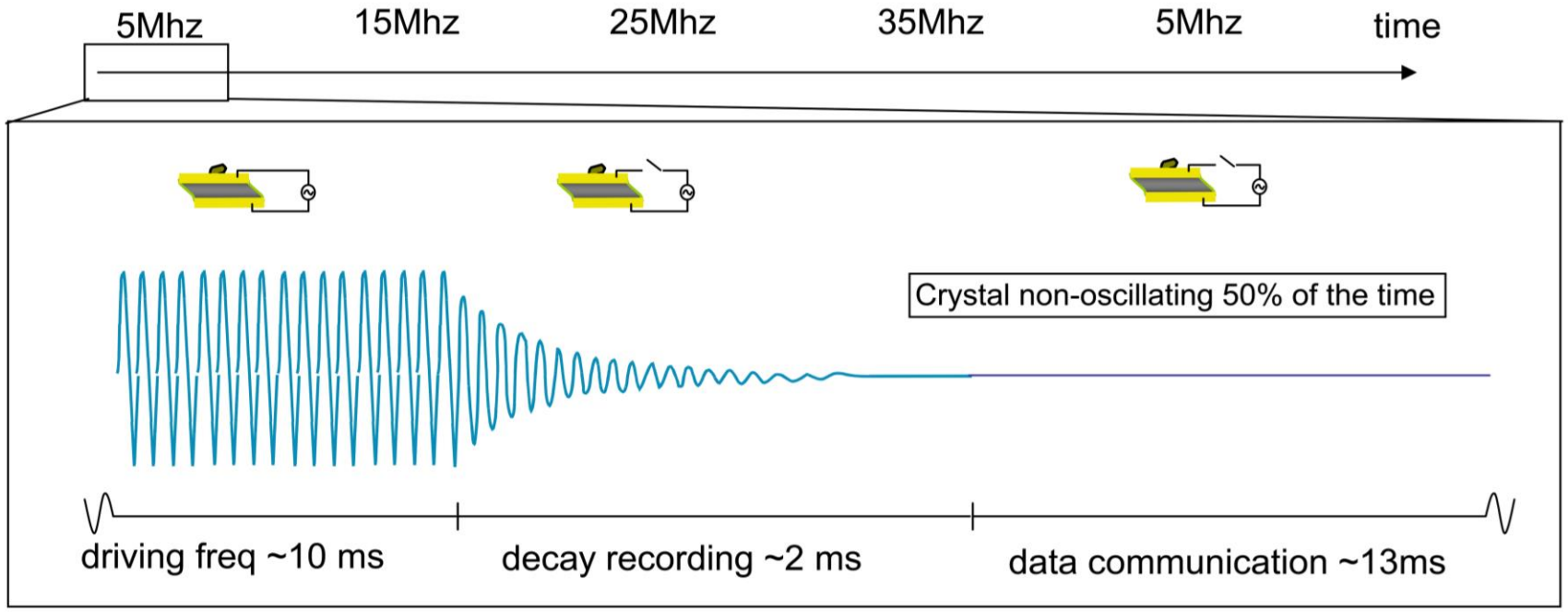
d

Eddaif, L., et al. Water, Air, & Soil Pollution (2019), doi.org/10.1007/s11270-019-4322-7

HM DETECTION STUDIES (QCM-I PRINCIPLE)

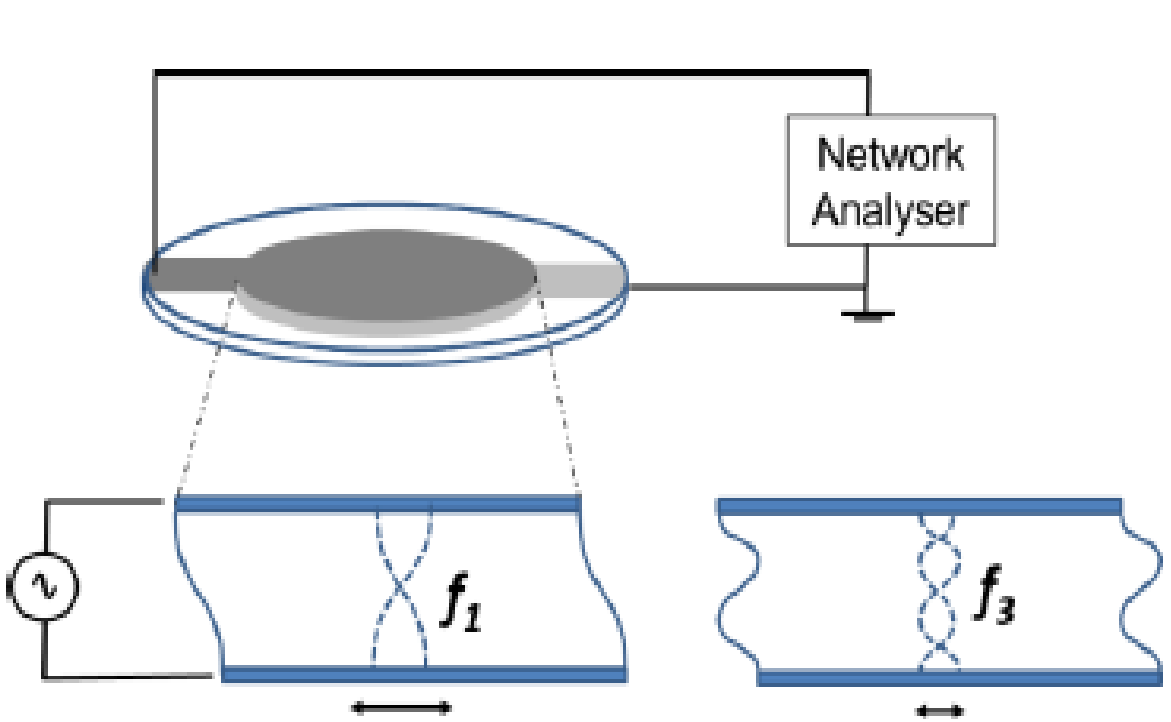
Features

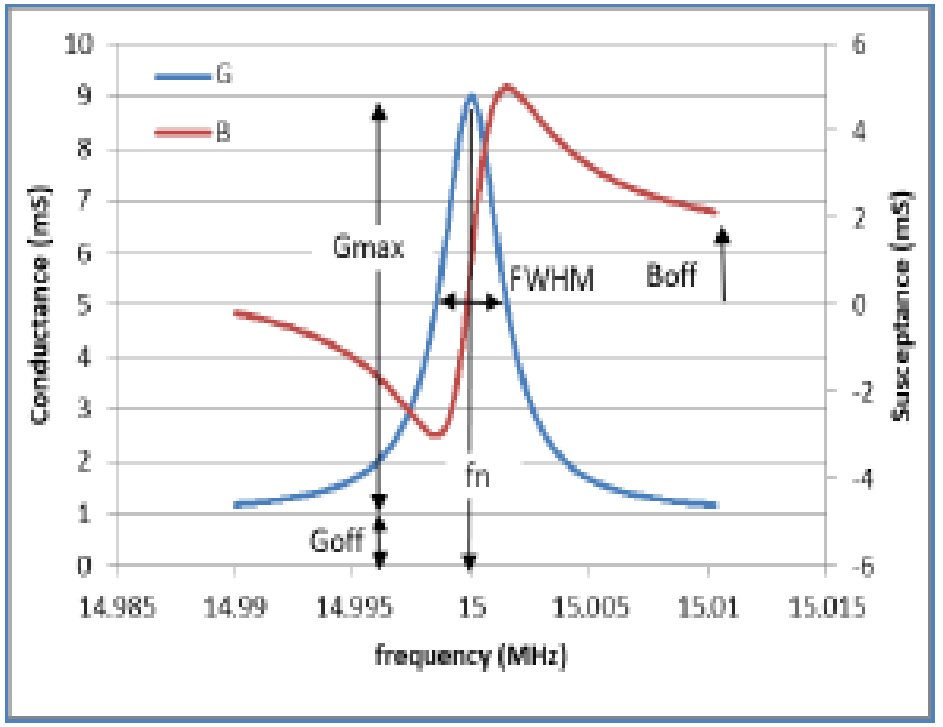
- Sequential multi frequency measurement
- Freely oscillating crystal=true crystal frequency
- Enables multiple frequencies & viscoelastic modeling



Note: QCM-D can sample viscoelastic changes over 200 times/sec.

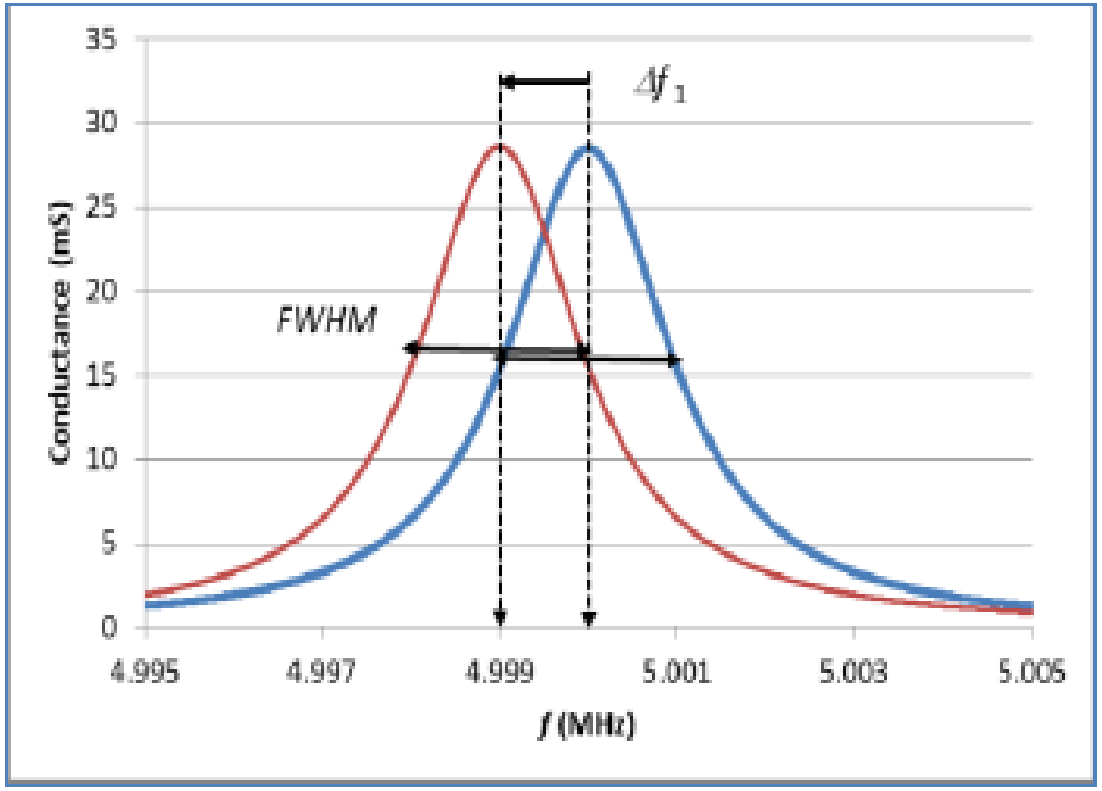
HM detection studies (QCM-I principle)

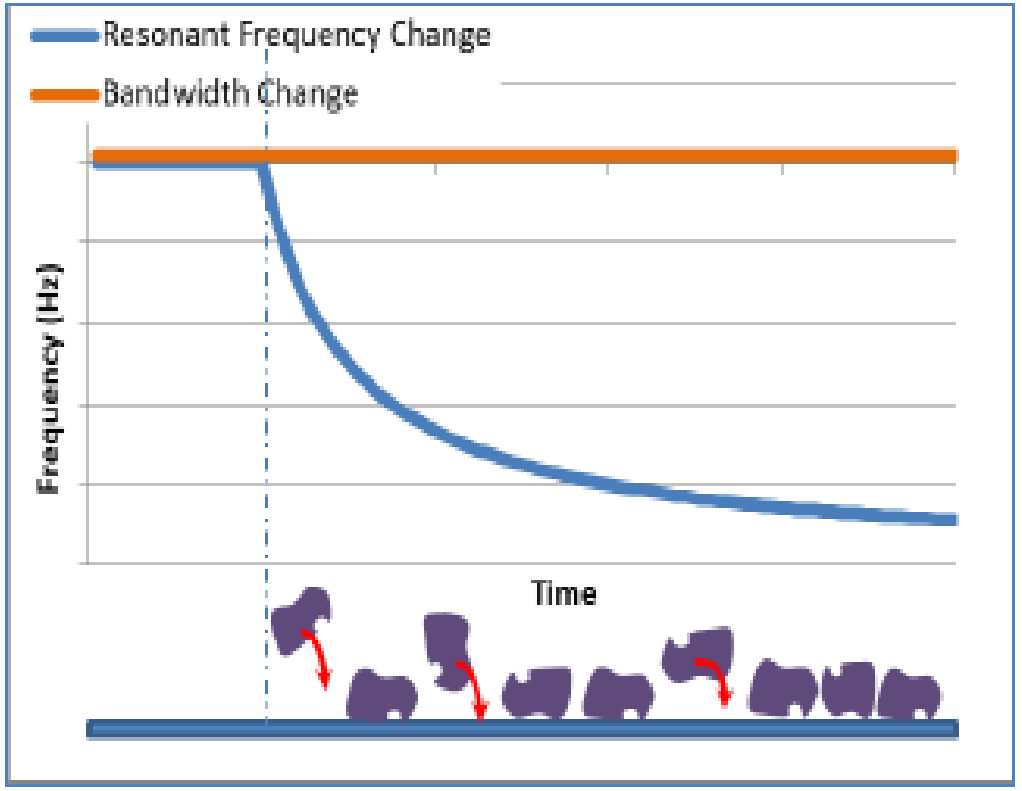




Schematic diagram of a quartz crystal sensor resonating at the fundamental and 3rd overtone frequency (left), and complex impedance spectrum vs. frequency (f3) with parameters fitted to the raw data (right).

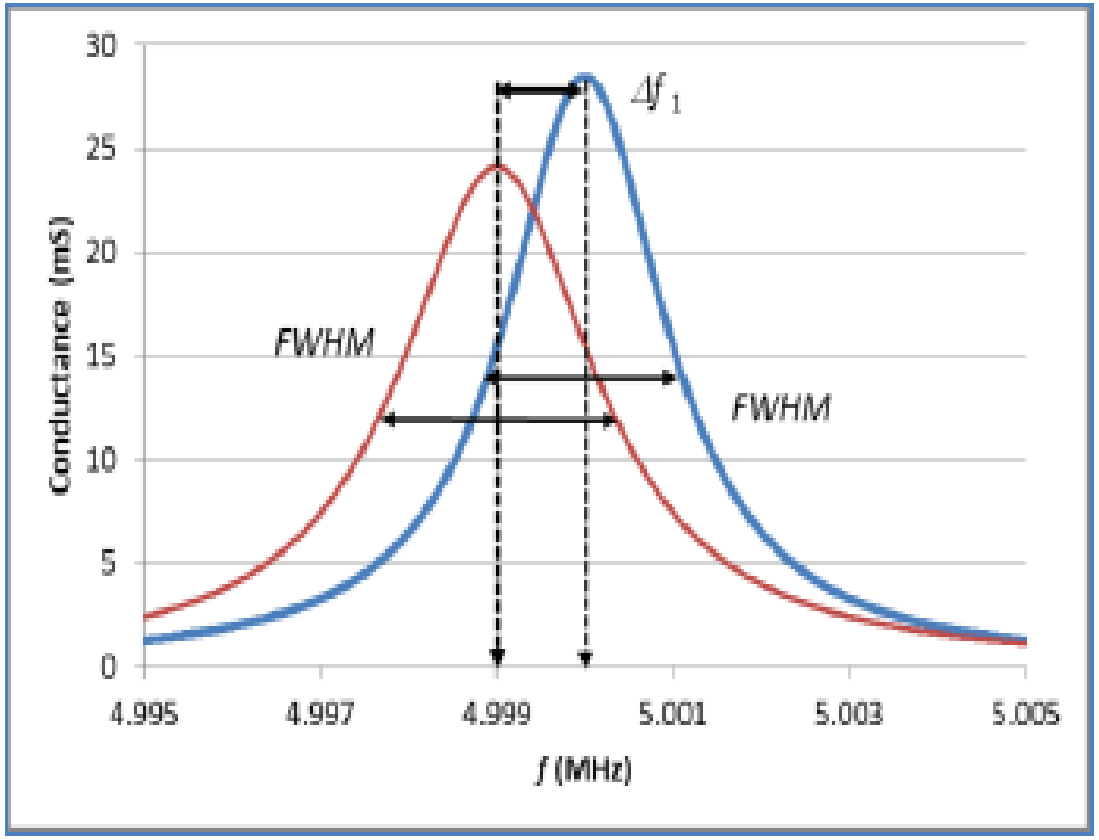
HM DETECTION STUDIES (QCM-I PRINCIPLE)

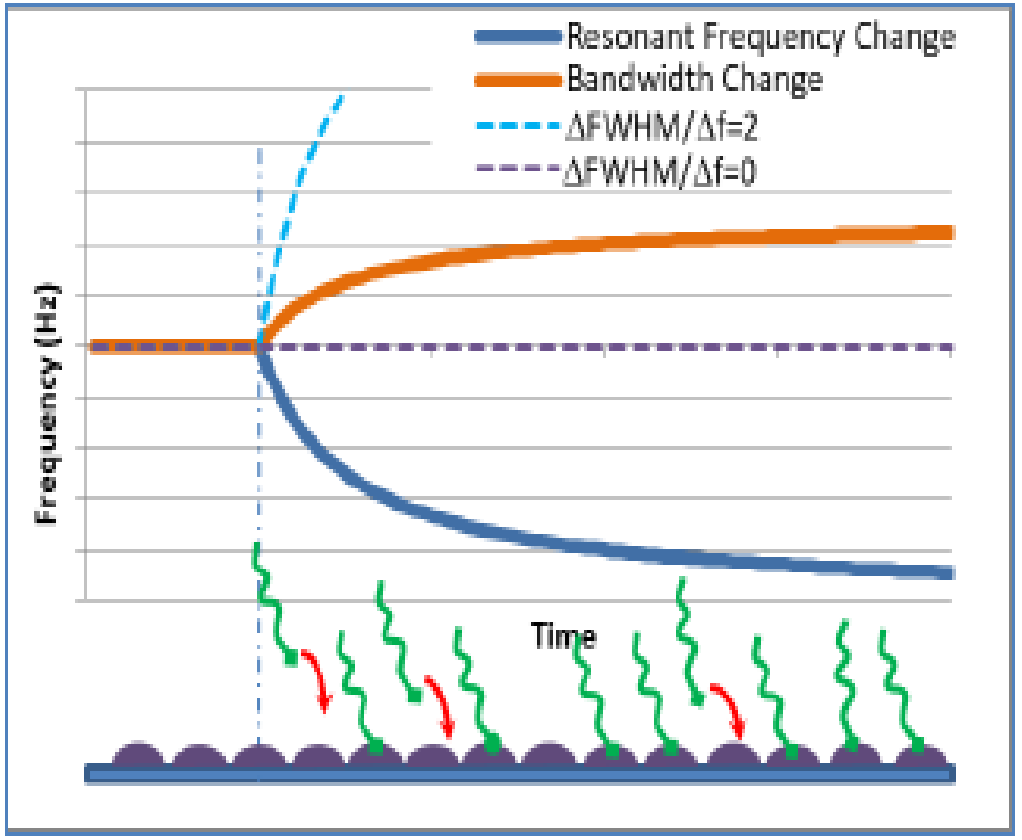




DIAGRAMS OF THE CHANGE IN CONDUCTANCE CURVE (N= 1 FOR A 5MHZ CRYSTAL), RESONANT FREQUENCY AND BANDWIDTH ON DEPOSITION OF A RIGID FILM ONTO THE SENSOR SURFACE

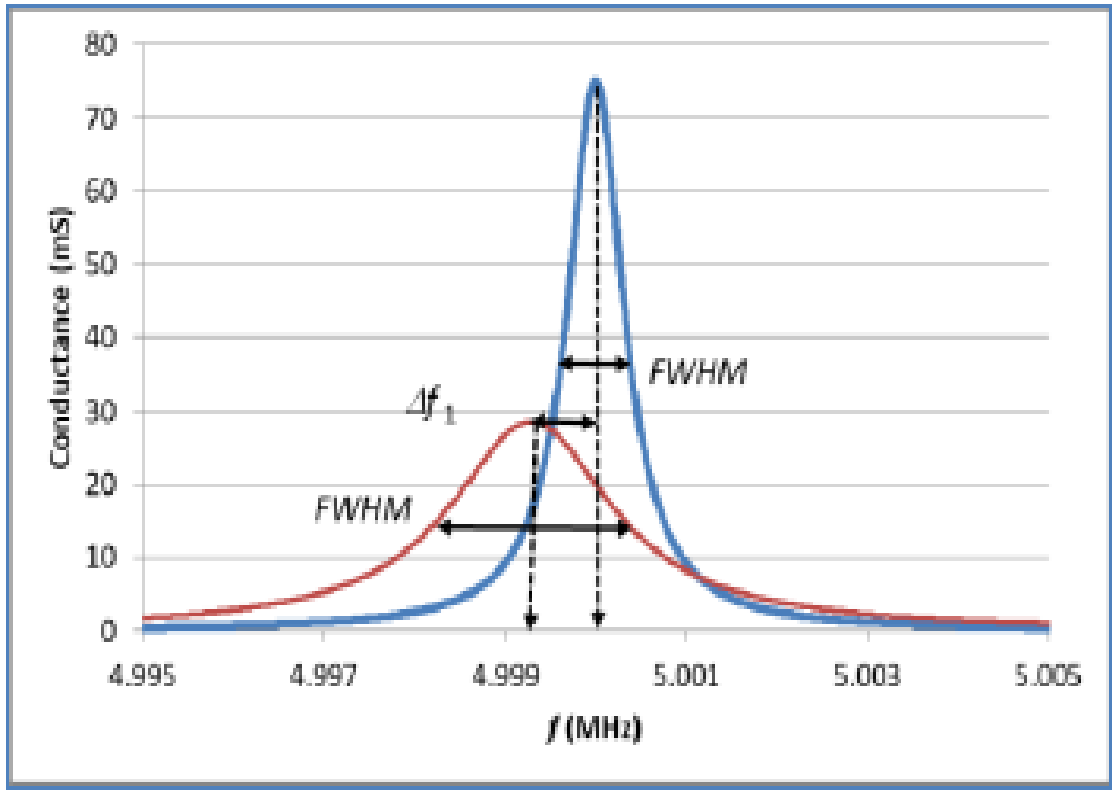
HM DETECTION STUDIES (QCM-I PRINCIPLE)

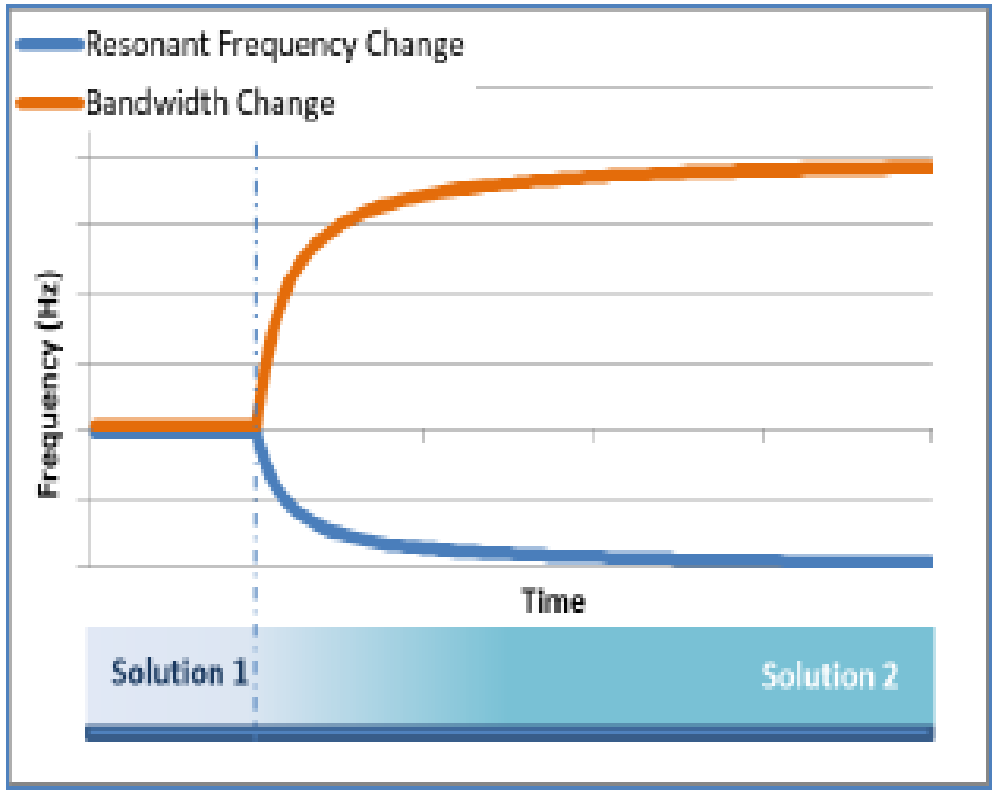




DIAGRAMS OF THE CHANGE IN CONDUCTANCE CURVE, RESONANT FREQUENCY AND BANDWIDTH FOR THE DEPOSITION OF A VISCOELASTIC LAYER ON THE SENSOR SURFACE.

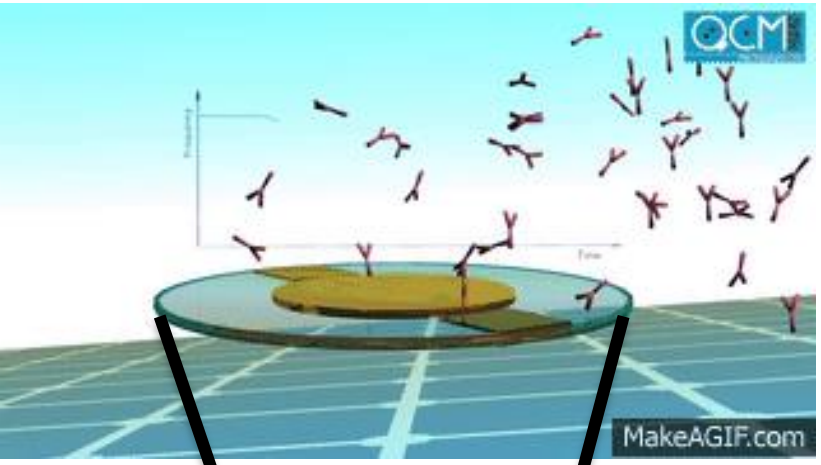
HM DETECTION STUDIES (QCM-I PRINCIPLE)

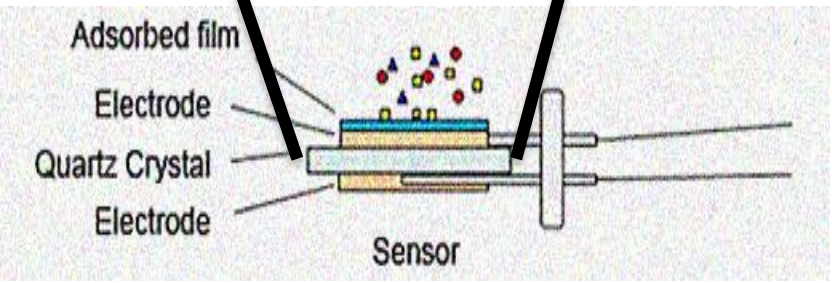




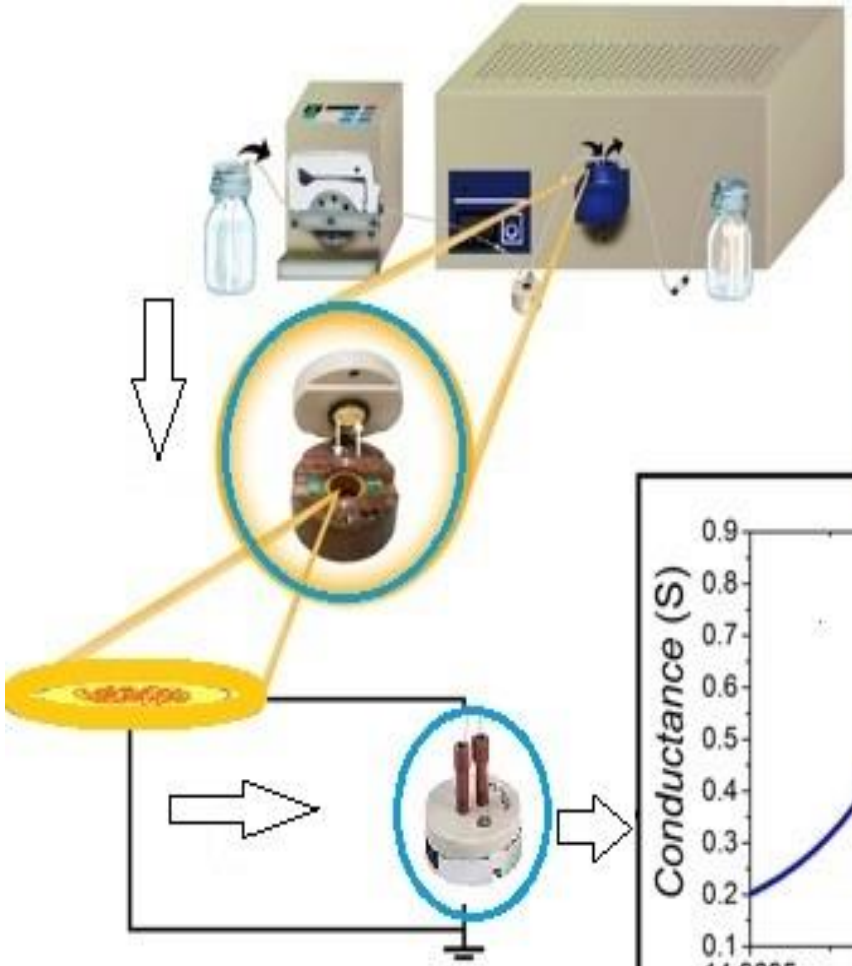
DIAGRAMS OF THE CHANGE IN CONDUCTANCE CURVE, RESONANT FREQUENCY AND BANDWIDTH FOR A CHANGE OF SOLUTIONS WITH DIFFERENT VISCOSITIES

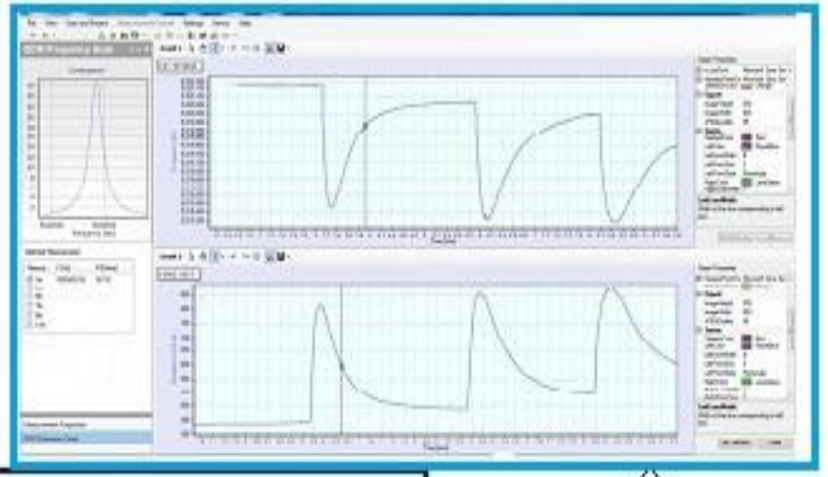
HM DETECTION STUDIES (QCM-I PRINCIPLE)

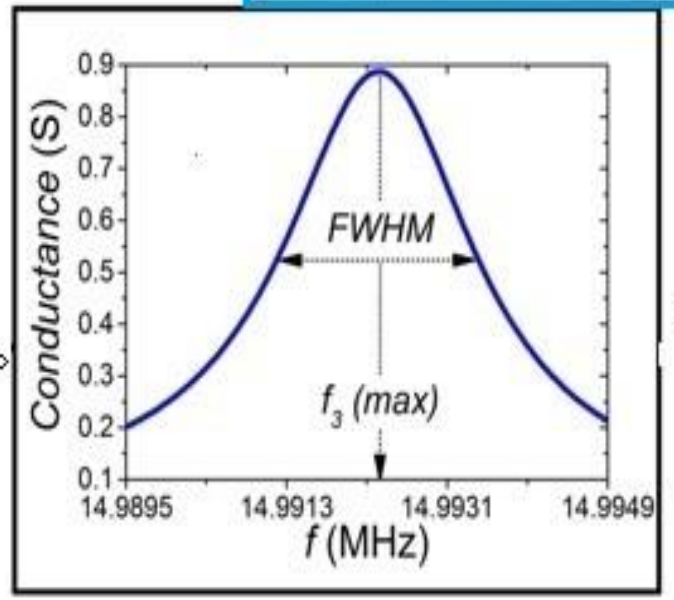




Frequency changes according to adsorption of chemicals on the QCM Surface



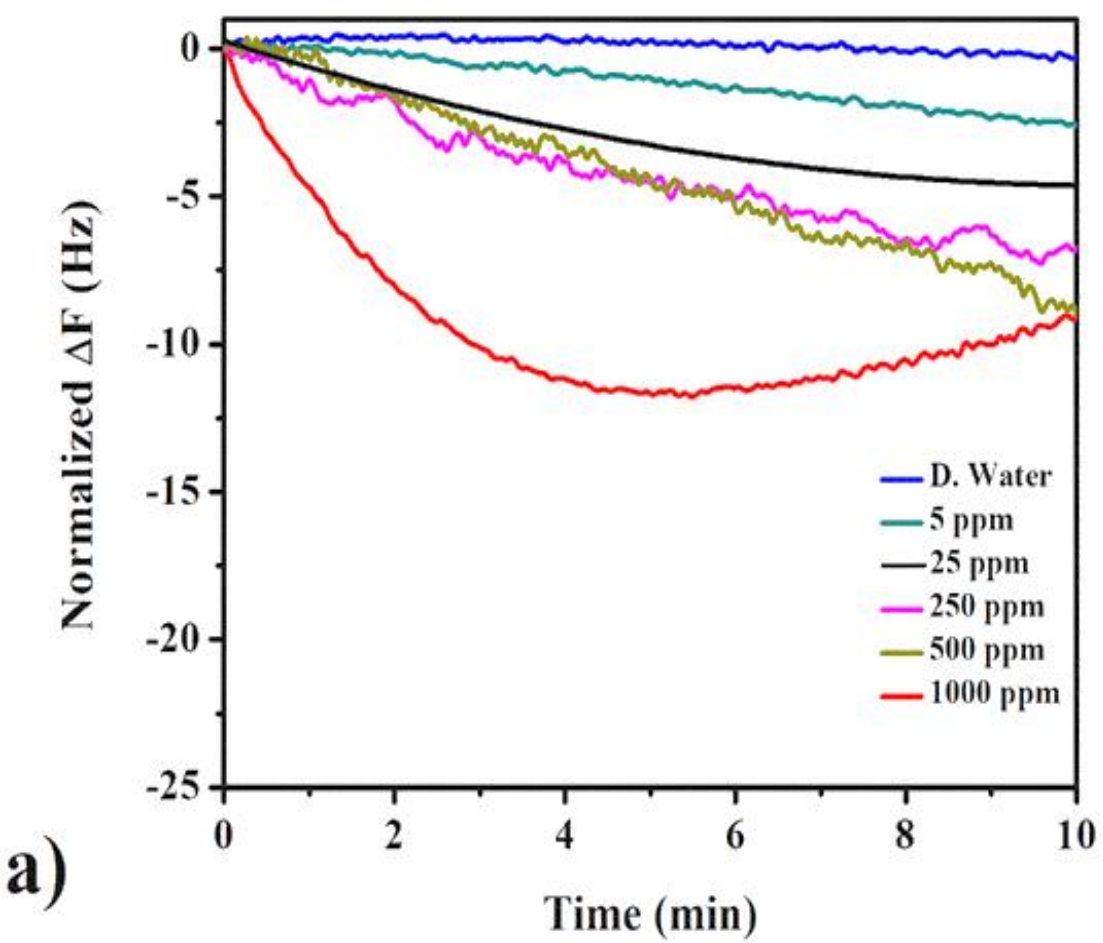




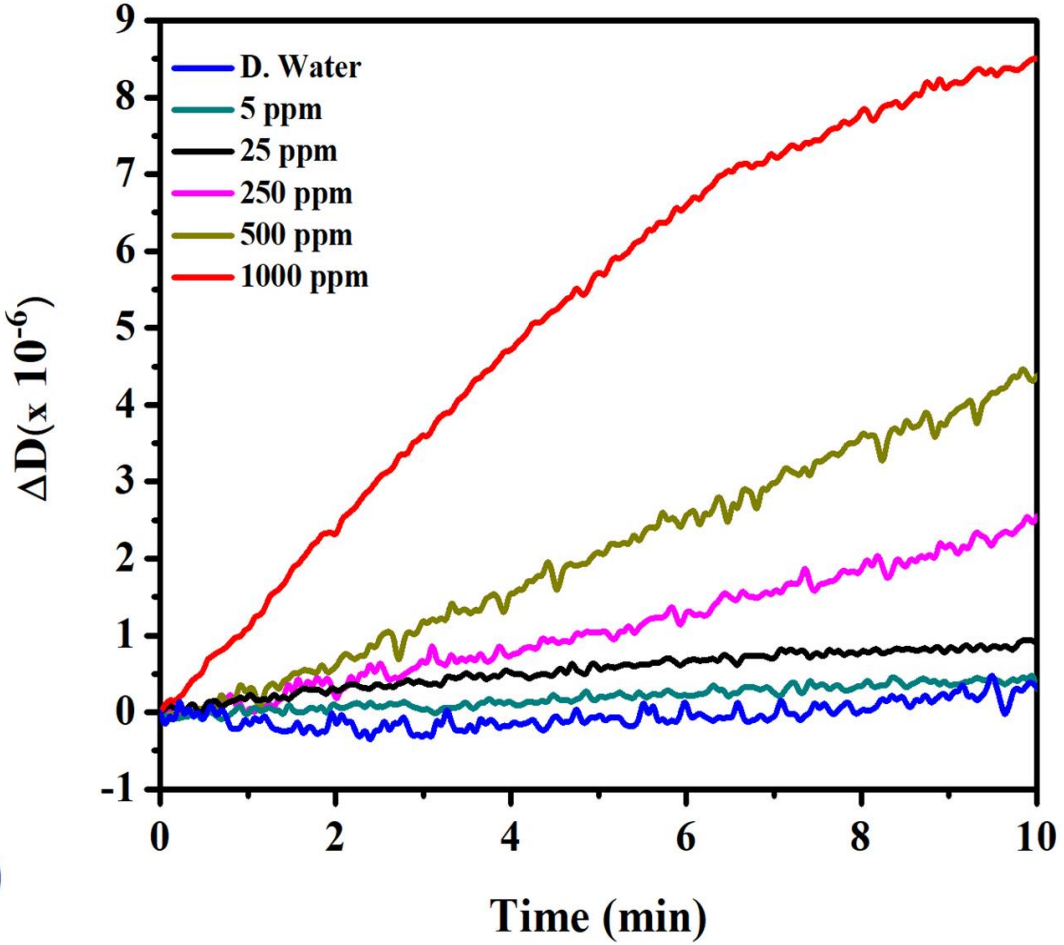
Output data
F, D, FWHM
Gmax,Goffs
Boffs, Fi,
Residual, Q,
T, Res
for n Over-
tones.

ΔF & ΔD Studies

Frequency (a) and dissipation shifts (b) of compound B based QCM sensor



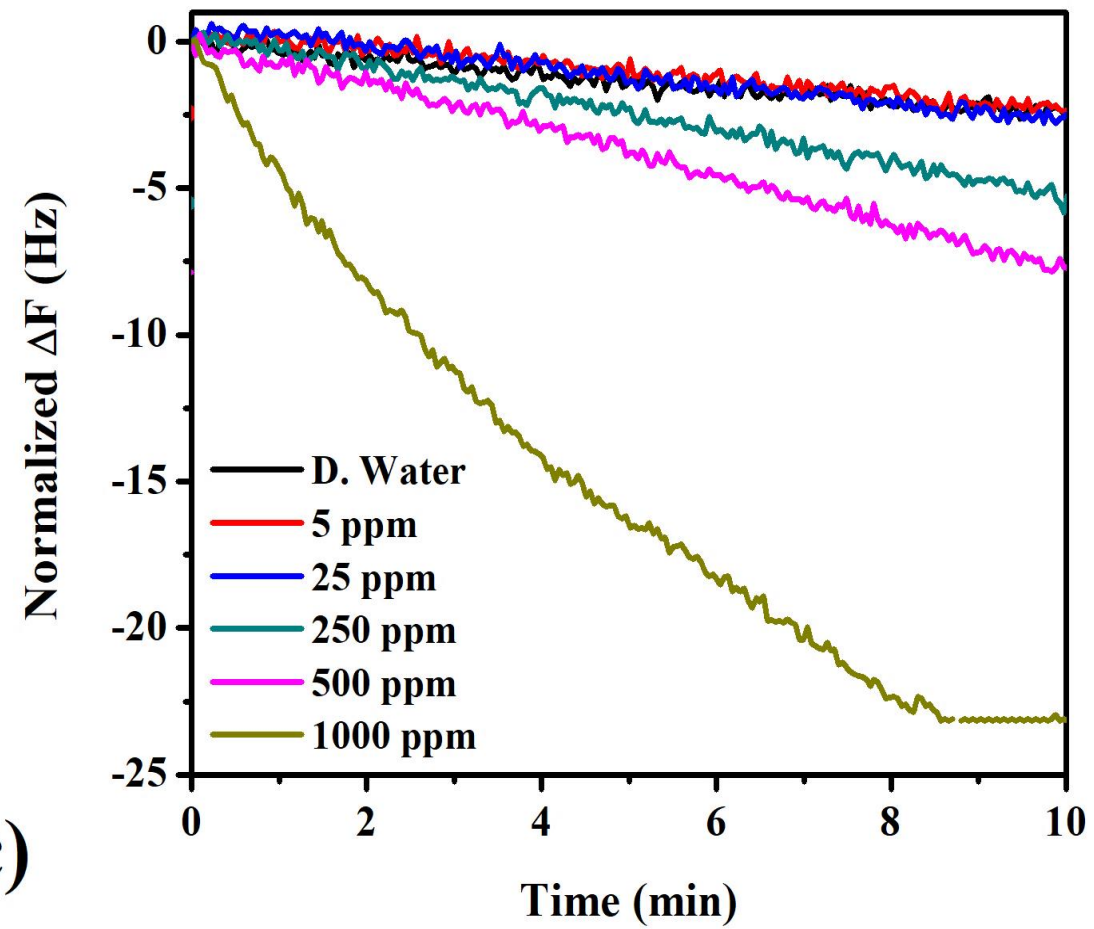
a)



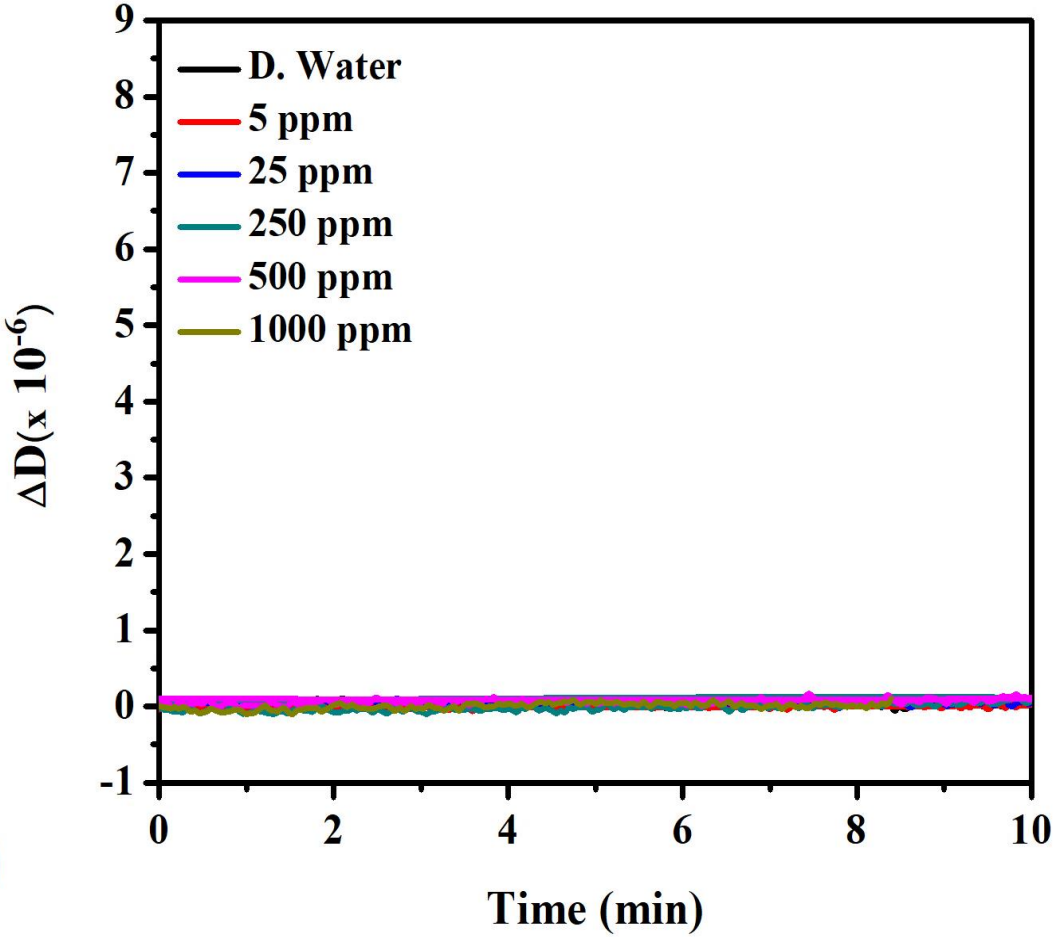
b)

ΔF & ΔD Studies

Frequency (a) and dissipation shifts (b) of compound C based QCM sensor



c)



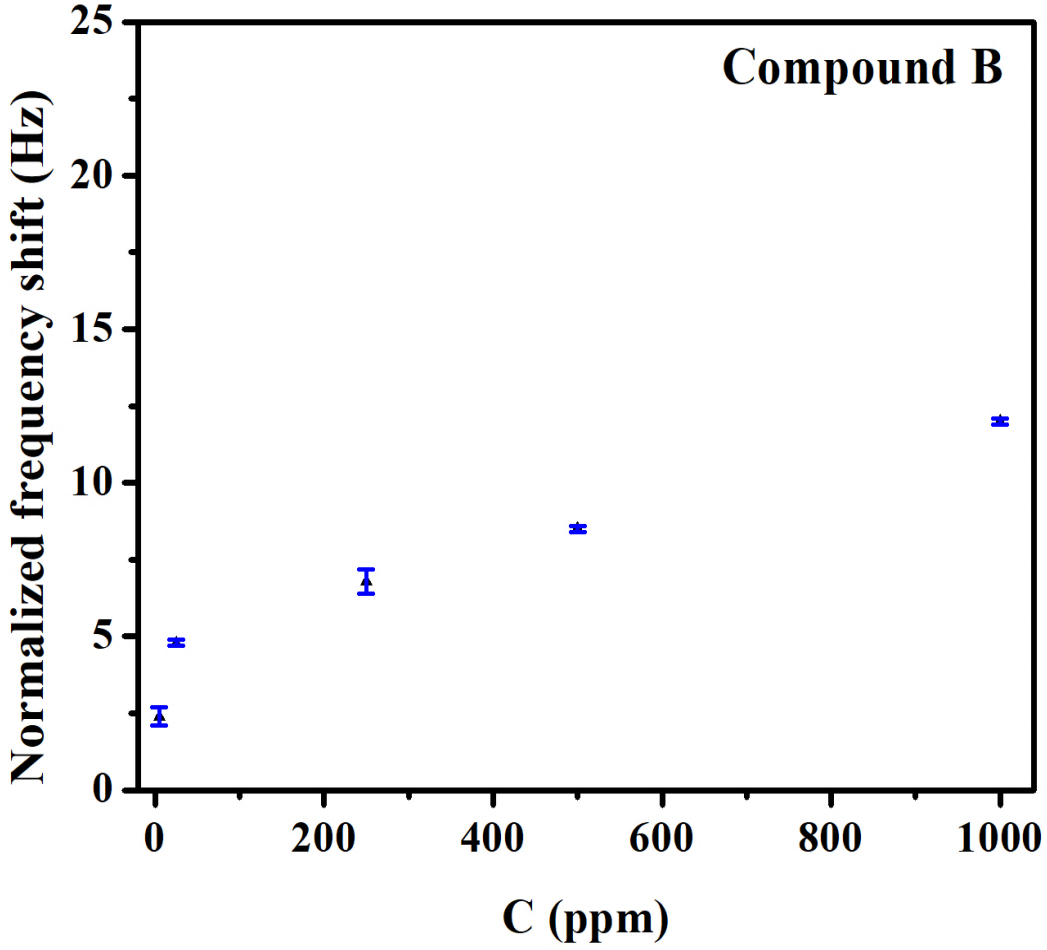
d)

Normalized frequency and dissipation energy shifts for compounds B and C at various Pb^{2+} concentrations.

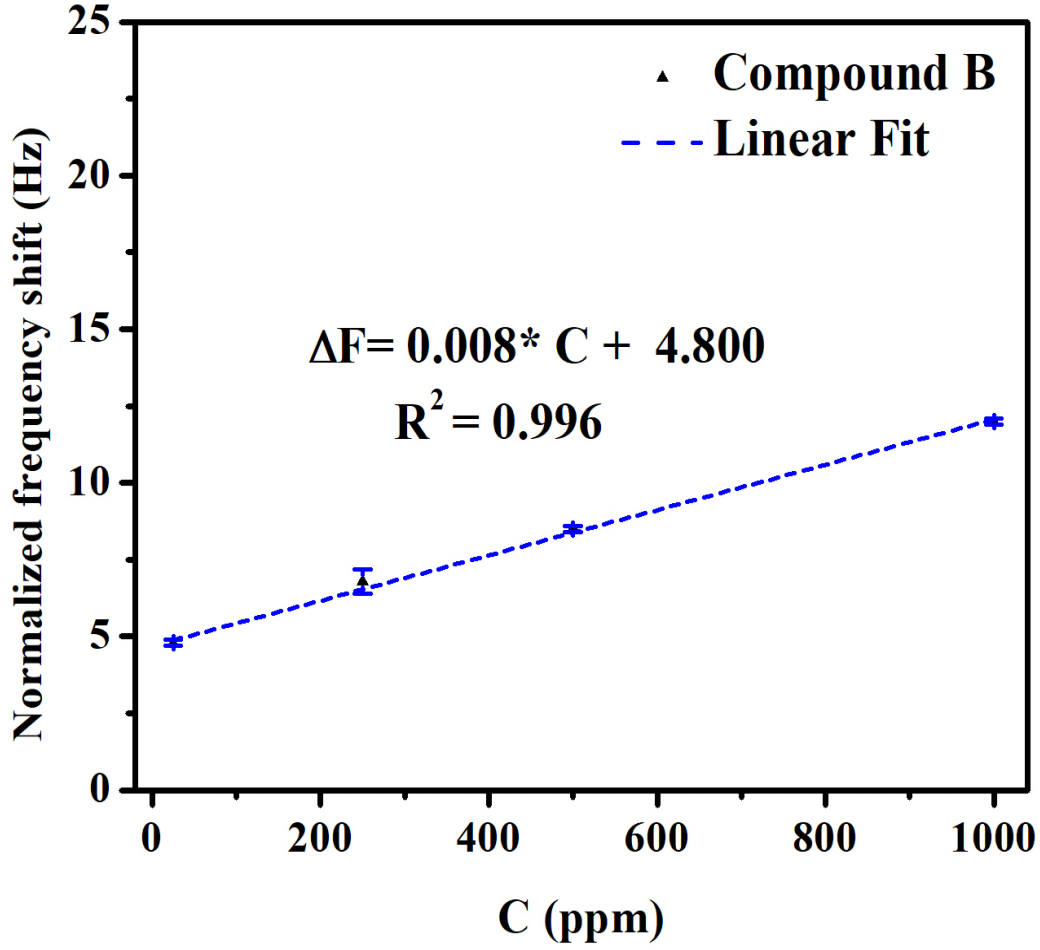
* Values are presented as average ± standard deviation

Measured value	Concentrations (ppm)	Compound B*	Compound C*
$\Delta F_n/n$ (Hz)	Blank (D. water)	- 0.30 ± 0.04	- 1.20 ± 0.10
	5	- 2.40 ± 0.30	- 2.50 ± 0.30
	25	- 4.80 ± 0.10	- 2.86 ± 0.04
	250	- 6.80 ± 0.40	- 5.72 ± 0.70
	500	- 8.50 ± 0.10	- 7.85 ± 0.40
	1000	- 10.00 ± 0.10	- 23.00 ± 0.01
ΔD_n (10^{-6})	Blank (D. water)	0.47 ± 0.23	0.10 ± 0.03
	5	0.54 ± 0.11	0.10 ± 0.01
	25	1.10 ± 0.34	0.21 ± 0.09
	250	2.50 ± 0.48	0.13 ± 0.01
	500	4.10 ± 0.23	0.11 ± 0.01
	1000	8.50 ± 0.07	0.10 ± 0.02

Obtained calibration curve for the Calix-QCM based sensor in the Pb^{2+} concentration range of 5-1000 ppm for compound B (a). Linear range(b)

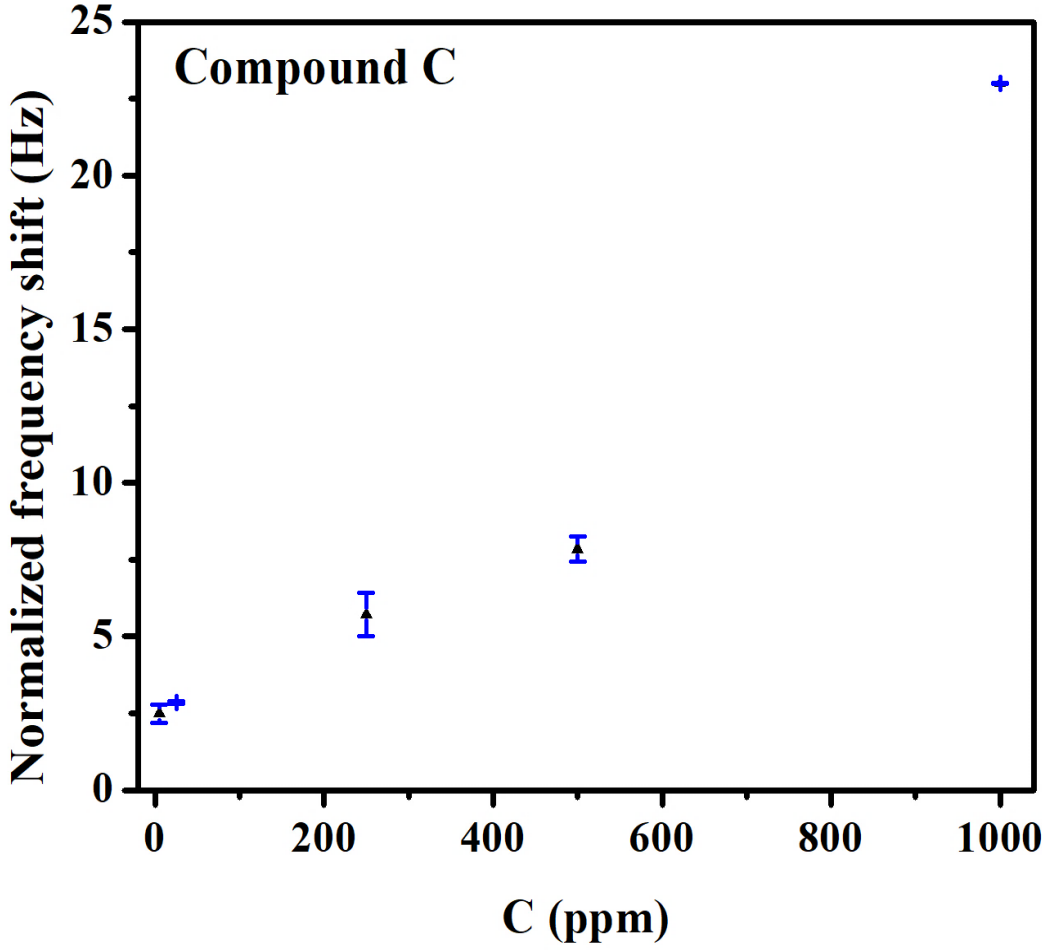


a)

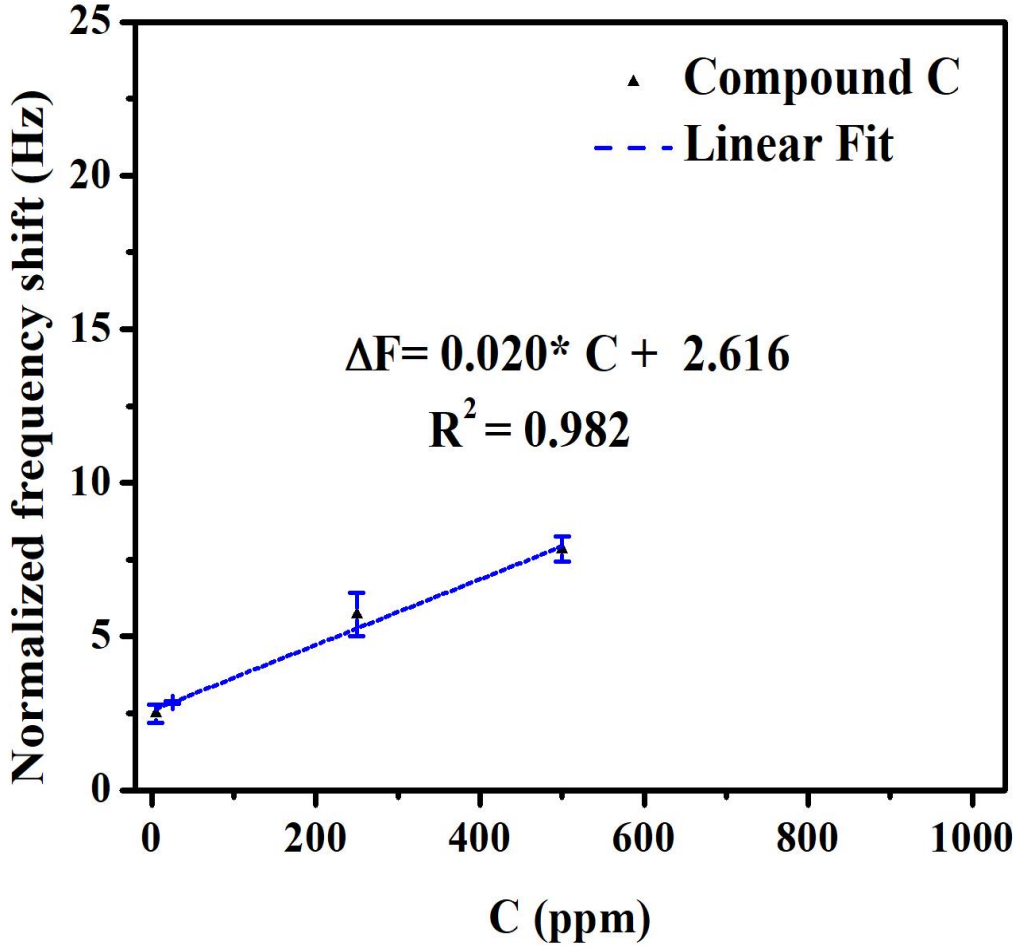


b)

Obtained calibration curve for the Calix-QCM based sensor in the Pb^{2+} concentration range of 5-1000 ppm for compound C (c). Linear range(d)



c)



d)

Sensing characteristics of compounds B and C based sensor platforms against different HM

	Compound B				Compound C			
HM ions	LR ppm	Sensitivity Hz.ppm^{-1}	LOD ppm	LOQ ppm	LR ppm	Sensitivity Hz.ppm^{-1}	LOD ppm	LOQ ppm
Cd^{2+}	3-1000	0.009	0.89	2.96	4-250	0.009	1.10	3.66
Hg^{2+}	1-1000	0.038	0.20	0.66	2-250	0.110	0.65	2.16
Cu^{2+}	0.5-1000	0.030	0.11	0.36	0.5-250	0.033	0.16	0.53
Pb^{2+}	25-1000	0.008	0.45	1.50	5-500	0.020	0.30	1.00

Achievements

No.	Date	Type	Journal	IF
1	March 2019	Conference paper	Proceedings of the 1st Coatings and Interfaces Web Conference	____
2	November 2019	Conference paper	Proceedings of the International Joint Conference on Environmental and Light Industry Technologies	____
3	January 2019	Journal article	Journal of Thermal Analysis and Calorimetry, Springer nature	**2.471**
4	May 2019	Journal article (Review)	International Journal of Environmental Analytical Chemistry Taylor & Francis	**1.267**
5	September 2019	Journal article	Arabian Journal of Chemistry Elsevier BV	**3.298**
6	November 2019	Journal article	Water, Air and Soil Pollution Springer Nature	**1.774**
7	December 2019	Journal article	Electroanalysis Wiley Online Library	**2.691**

Conferences/ Seminars

Conference/ Seminar	Location/ Year	Oral/Poster presentation	Conference achievement
1st Coatings and Interfaces Web Conference	Italy March 2019	Oral presentation	Conference paper
ForMilk summer school (at the Research Centre for Natural Sciences)	Budapest, May 2019	____	____
Matrafured International Meeting on Chemical Sensors	Visegrad, June 2019	Poster presentation	Journal article
TTK AKI seminar (at the Research Centre for Natural Sciences)	Budapest, October 2019	Oral presentation	____
Workshop on Environmental Sciences and Engineering (International Joint Conference on Environment and Light Industry Technologies)	Budapest, November 2019	Oral presentation	Conference paper

Future work

To carry on the surface layer characterization (***AFM***) and (***ESEM***);

To perform EC detection measurements using methods as (***CV***) and (***EIS***), as well, to carry out simultaneous detection tests using (***SWASV***) …etc.,

And, to continue the ***QCM*** detection tests.

Thank You For Your Attention.

Happy To Answer Any Questions.