# Comparison between High Fundamental Frequency Quartz Crystal Microbalance and Love Mode Surface Acoustic Wave devices in the detection of Carbaryl pesticide


**J.V. García[1,4*], M.I. Rocha[1,4*], C. March[2,4], P. García[1,4], L. Francis[3], A. Montoya[2], A. Arnau[1], Y. Jiménez[1]**

[1]Grupo de Fenómenos Ondulatorios (GFO), Universitat Politècnica de València, Valencia, Spain
[2]Grupo de Inmunotecnología, I3BH-UPV, Universitat Politècnica de València, Valencia, Spain
[3]Sensors, Microsystems and Actuators Laboratory of Louvain (SMALL), Université catholique de Louvain, Belgium
[4]Advanced Wave Sensors S.L., Valencia, Spain.


## Abstract


In this work two acoustic technologies: High Fundamental Frequency Quartz Crystal Microbalance (HFF-QCM) and Love Mode Surface Acoustic Wave (LM-SAW) have been compared for the detection of Low Molecular Weight (LMW) compounds in terms of Sensitivity and LOD. The results have also been compared with those obtained with other techniques: Traditional QCM, Surface Plasmon Resonance (SPR) and Enzyme-Linked ImmunoSorbent Assay (ELISA). Carbaryl pesticide was chosen as model analyte because it had been used as a reference LMW compound by those mentioned techniques.
A-10 research platform (AWSensors, Spain) was used to perform the experiments. This platform allowed for a comparison of both devices measured by the same characterization system under similar experimental conditions.
The results achieved with LM-SAW and 100MHz HFF-QCM are in the same order of magnitude. The achieved sensitivity ($I_{50}$ value) and LOD ($I_{90}$ value) were around 0.31 µg/L and 0.09 µg/L, respectively, for LM-SAW device, and around 0.66 µg/L and 0.14 µg/L, respectively, for HFF-QCM device. Sensitivities and LODs with this novel developments on acoustic technologies improve SPR and traditional QCM technologies, and approaches ELISA's ones.


## High Resolution Technique

- European regulatory levels demand very low LODs of pesticide in water intended for human consumption (0,1µg/L).

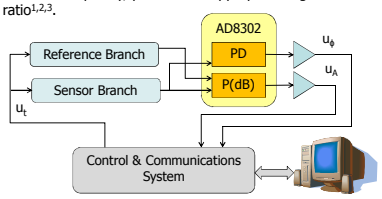
**IMPROVEMENT OF LOD**

$$LOD = \frac{3 \cdot N}{S}$$

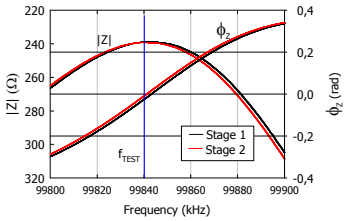
- $N$ → By reducing the noise of the read-out system
- $S$ → By increasing the sensor sensitivity

**ELECTRONIC CHARACTERIZATION SYSTEM IN RP A-10**

- Differential system, based on a phase mass measurement at constant frequency, provides an appropriate Signal-to-Noise ratio[1,2,3].




- Impedance spectrum variation with a sample injection of 0.001 µg/L of Carbaryl




**THEORETICAL SENSITIVITIES**

| | QCM 10MHz | HFF-QCM 50MHz | HFF-QCM 100MHz | LM-SAW 120MHz |
|---|---|---|---|---|
| $\Delta\varphi/\Delta\sigma\,(\mathrm{rad\cdot m^2\cdot kg^{-1}})$ | -10,687 | -22,593 | -30,697 | -10,617 |
| $(1/f_0)(\Delta f/\Delta\sigma)(\mathrm{m^2\cdot kg^{-1}})$ | -2.27 | -11.33 | -22.67 | -17.05 |

f: Frequency φ: Phase
$f_0$: Reference frequency σ: Surface mass density

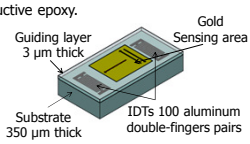
## Experimental

**100 MHz HFF-QCM SENSORS**

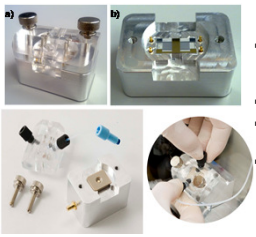
- 100 MHz HFF-QCM inverted mesa resonators (electrode Ø = 1mm) bonded permanently to a PEEK support by an epoxy adhesive. Electrical contact between resonator electrodes and copper pads by conductive epoxy.

**120 MHz LM-SAW SENSORS**

- Specifically designed and fabricated for the flow cell 120 MHz $SiO_2$/AT-cut quartz Z propagating LW device with IDTs periodicity 40 µm.



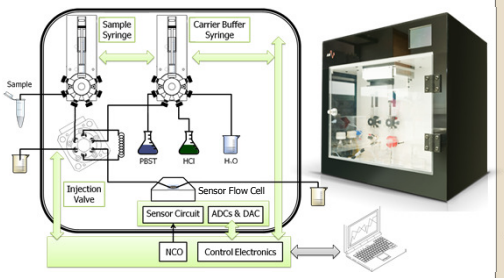

**LM-SAW / HFF-QCM FLOW CELLS**




- User friendly flow cells allow a fast and easy installation and replacement of the sensors.
- Mechanical, thermal, electrical and chemical requirements were considered.
- Lower part: Aluminium.
- Upper part: PMMA allows visibility to the sensing area of the devices.
- PDMS sealant between sensor device and upper flow structure creates a chamber of around 4 µL in LM-SAW Cell and 2,75 µL in HFF-QCM Cell.

**MEASUREMENT SET-UP: RESEARCH PLATFORM A-10**

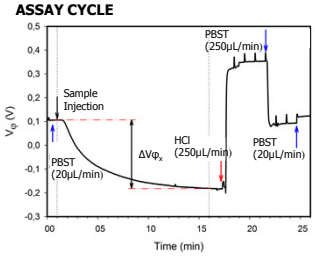
- Platform consists on an automated flow injection system with automated syringe pumps, distribution and injection valves; sensors flow cells; sensors characterization circuit; remote control and communication electronics and data acquisition program .
- Temperature inside black box was maintained constant at 25º±0.05ºC.




**IMMUNOASSAY FORMAT. CARBARYL DETECTION**

- Competitive immunoassay. Inhibition test based on conjugate coated format.
- Sensor functionalization: Carbaryl hapten conjugate BSA-CNH covalently immobilized, via mercaptohexadecanoic acid (MHA) Self Assembled Monolayer (SAM).

**ASSAY CYCLE**

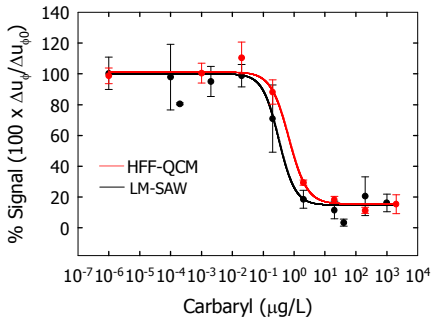



- Assay cycle includes surface regeneration.
- Real time monitoring of voltage associated to phase shift variation due to hapten conjugate-antibody binding.

## Results

**STANDARD CALIBRATION CURVES**

| [BSA-CNH] | [Mab] LIB-CNH45 | SAMPLES |
|---|---|---|
| 10 µg/mL | 2 µg/mL | [Carbaryl]+2 µg/mL LIB-CNH45 MAb in PBS |




- EXPERIMENTAL POINTS FITTING

$$y = D + \frac{A-D}{1+\left(\frac{x}{C}\right)^B}$$

$x$=[Carbaryl]
$y$=% Signal

| | HFF-QCM | LM-SAW |
|---|---|---|
| I90 (µg/L) | 0,14 | 0,09 |
| I50 (µg/L) | 0,66 | 0,31 |
| I80-I20 (µg/L) | 0,26-1,73 | 0,14-1,63 |

**SENSITIVITY PARAMETERS OBTAINED WITH DIFFERENT TECHNOLOGIES IN CARBARYL IMMUNOASSAY DETECTION**

| | ELISA[4] | SPR[5] | QCM 9MHz[6] Δf | QCM 10MHz[7] Δφ | HFF-QCM 50MHz[8] Δφ | **HFF-QCM 100MHz Δφ** | **LM-SAW 120MHz Δφ** |
|---|---|---|---|---|---|---|---|
| Sensitivity (µg/L) | 0,22 | 3,12 | 30,34 | 16,7 | 1,95 | **0,66** | **1,28** |
| LOD (µg/L) | 0,05 | 1,41 | 13,30 | 4,00 | 0,23 | **0,14** | **0,27** |
| Working Range (µg/L) | 0,08-1,1 | 1,91-5,75 | 18.30-50,30 | 7,00-35,00 | 0,50-7,20 | **0,26-1,72** | **0,48-3,30** |

## Conclusion and References

A comparison between HFF-QCM and LM-SAW for the detection of the LMW compound Carbaryl pesticide has been carried out. This comparison has been done in the same conditions by using the research platform A-10 (AWSensors, Spain). Compared with traditional QCM (10MHz) results reported by our group, an improvement of two orders of magnitude in sensitivity and LOD was achieved with both technologies. The obtained values of sensitivity and LOD exceed in one order of magnitude those obtained with SPR and approaches those for ELISA.
The present results suggest that in a near future both acoustic devices could allow the detection of Carbaryl compound in water intended for human consumption at European regulatory levels.

**REFERENCES**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*Contact: yojiji@eln.upv.es ; awsensors@awsensors.com*