Article

Journal Industrial Engineering
June 2023, Vol.7 No.18 34-41

Preliminary Development of an upgrade of a chamber to measure the response of quartz crystal resonators

Desarrollo preliminar de la actualización de una cámara de medición de respuesta de sensores de gas de cristal de cuarzo

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DOI: 10.35429/JIE.2023.18.7.34.41

Received January 25, 2023; Accepted June 30, 2023

Abstract

Quartz crystal microbalance (QCM) sensors have been frequently used as weighing devices, since they have proven to be sensitive due to shifts in their resonant frequency due to increments in the mass attached to their surface. These, are normally used as sensor arrays for systems known as "Electronic Noses", to detect and analyze gases, fluids, medical and environmental applications, and biological compounds, among others. For the implementation of such systems, it is necessary to characterize the response of the sensors at different types of compounds, primarily in temperature-controlled environments, which implies the use of control systems with a high cost. This work presents the preliminary design of a static system to measure the response of quartz crystal gas sensors, as a lower cost proposal, using an open-loop controlled temperature environment, through an electronic communication system with the computer and a virtual instrumentation software to monitoring and manipulating the temperature. To observe the effectiveness of the system, real QCM gas sensors with a coat of sensing film of ethyl cellulose were used, applying concentrations of ethanol. In addition, temperatures of 25°C, 35°C and 45°C were adjusted, obtaining typical results of the response of this type of sensors.

QCM, Electronic Nose, Microcontrollers

Resumen

Los sensores de micro balanza de cristal de cuarzo (QCM) se han empleado frecuentemente como dispositivos de pesaje, puesto son altamente sensibles debido a corrimientos en su frecuencia de resonancia generados por incrementos en la masa adherida sobre su superficie. Estos, son usados como arreglos de sensores para sistemas conocidos como “Narices Electrónicas”, para detección y análisis de gases, fluidos, aplicaciones médicas, ambientales, compuestos biológicos, entre otros. Para implementar dichos sistemas es necesario caracterizar las respuestas de los sensores a diferentes compuestos, principalmente en ambientes de temperatura controlados, lo que implica el uso de sistemas de control con un alto costo. Este trabajo presenta el diseño preliminar de un sistema estático para medir la respuesta de sensores gas de cristal de cuarzo, como una propuesta a menor costo, usando ambiente de temperatura controlado en lazo abierto, a través de un sistema electrónico de comunicación con una computadora y software de instrumentación virtual para monitorear y manipular la temperatura. Para observar la efectividad del sistema se usaron sensores de gas QCM reales con película sensible de etíl celulosa aplicando concentraciones de etanol. Además, se ajustaron temperaturas de 25°C, 35°C y 45°C obteniendo resultados típicos de la respuesta de este tipo de sensores.

QCM, Nariz Electrónica, Microcontroladores

Citation: LOPEZ-RAMIREZ, Carlos Alberto, MUÑOZ-MATA, José Lorenzo, ROJAS-GARNICA Juan Carlos and CERVANTES-DE LA ROSA, Juan Pedro. Preliminary Development of an upgrade of a chamber to measure the response of quartz crystal resonators . Journal Industrial Engineering. 2023. 7-18: 34-41

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Introduction

Electronic Noses had as a principal objective to replace to the expert panels in order to classified aromas for product testing, since such products were considered very expensive, difficult to transport and subjective, due to fatigue, mood, the weather and other external factors, could affect their evaluations. For this type of test support teams were used, such as gas chromatographs and mass spectrometers, in this case, to classifying and quantifying odors, with a high cost of production. Currently, electronic noses are used for the classification of aromas and odor detection that can be defined as: the emanation of emissions that matter radiates.

The electronic Nose applications have extended due to research in several fields. In agri-food industry had a great impact, helping to discriminate the degree of maturity of mangoes (Leburn, *et al*, 2008). In the monitoring of the environment, drinking water quality (Gardner *et a*l, 2000). In medicine, with the detection of volatile organic components detected through the breath as markers of lung cancer (Zhunan *et al*, 2003), and the detection of explosives in security systems (Edward J. Staples, 2007).

Quartz Crystal Microbalance Sensors (QCM) are very sensitive devices to small mass variations, due to the frequency shift in the resonant frequency of the quartz crystal. The Sauerbrey equation, describes the frequency shift on the sensor generated of the chance of the mass per unit on the electrode surface.

$$\Delta f = -2.3 \times 10^{-6} \cdot F^2 \frac{\Delta m}{A}, \quad (1)$$

Δf is the frequency shift, $2.3x10^{-6}$ is a constant with the characteristics of the density and shear module, Δm is the absorbed mass, and F is the resonant frequency of the crystal (Sauerbrey 1959).

The operation of the crystals is effective and precise for the detection of various volatile organic compounds, which contains a quartz disc with two electrodes placed on both sides of the disc. Quartz is a material that is considered piezoelectric (Shaukat H, *et al*, 2023), since it can convert mechanical tension into electricity, and electricity into mechanical vibrations through the inverse effect (piezoelectric effect). In addition, they are highly sensitive to changes in temperature and humidity.

In a previous work it had been reported by (Muñoz. *et al* 2019). Design and implementation of a gas response measurement system, however, they used a different measurement chamber, which is limited by design in scope of the temperature ranges. Moreover, the transfer of information rate is performed at least every 500 ms, which slows the process of acquisition and response of the system.

In this work we present a preliminary development of a gas sensor response measurement system, in this particular case, only for quartz sensors, therefore, a measurement chamber was designed with the objective of optimize the temperature range. On the other hand, it is proposed to improve the acquisition time and to be able to optimize the signal processing firmware. Finally, additional actuators were added in order to increase the response time of the system (Gardner *et al*, 2000). For the experimental results, the temperature was controlled using a PID close loop regulator. In addition, 12 MHz QCM gas sensors were built with a sensitive film of ethyl cellulose applying ethanol samples, where it could be observed that the system yields typical responses corresponding to the QCM sensors.

Experimental setup

Figure 1 shows the block diagram used for the implementation of the proposed system.

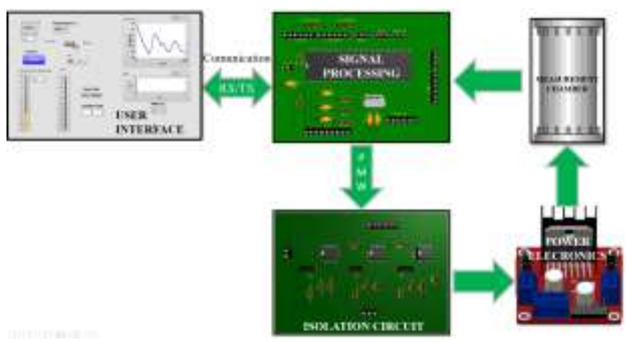

Figure 1 Block Diagram of the measurement system
Source: Self Made

As can be observed in Figure 1, the system consists of 5 stages: Control, Processing, Isolation, Power electronics and the camera.

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1.-Control System

LabVIEW software (Pineda-Olivares, 2018) was used to develop the user interface, through the RS-232 communications protocol using a data transfer rate of 9600 bauds per second and an acquisition and processing time of 100 ms, the information of the temperature sensor is received in order to monitoring and regulating the temperature of the interior of the measurement chamber. In this case, the digital sensor DS18B20 was used to measure the temperature with a resolution of 12 bits. Finally, the information is visualized numerically and graphically, as is shown in Figure 2.

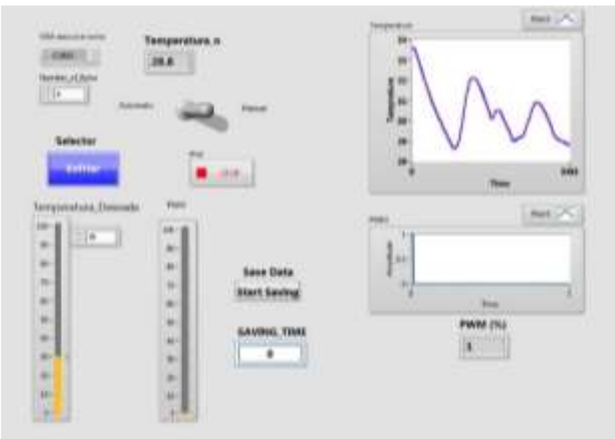

Figure 2 User interface of the system developed using LabVIEW
Source: Self Made

2.-Signal Processing

The transformation of the information is performed through the asynchronous serial communication protocol using the PL2303 converter module, between the control stage and the processing stage, using the PIC16F877A microcontroller (García, E. (2009), at a frequency clock of 4 MHz. PWM signals are used to regulate the power applied to the actuators. Figure 3 shows the flowchart that corresponds to the firmware developed within the microcontroller.

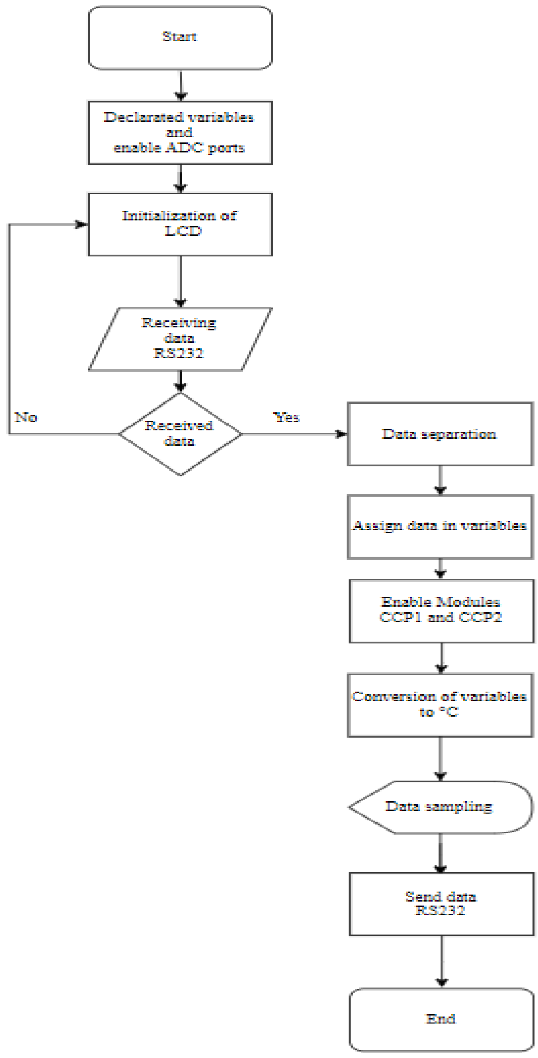

Figure 3 Flux diagram of the firmware development
Source: Self Made

3.-Isolation circuit

Figure 4 shows the circuit used to isolate the power electronics from the microcontroller using the optocouplers 4N25, in order to prevent a system failure in the microcontroller, additionally a transistor BC548 was used to maintain the current transfer of the signals.

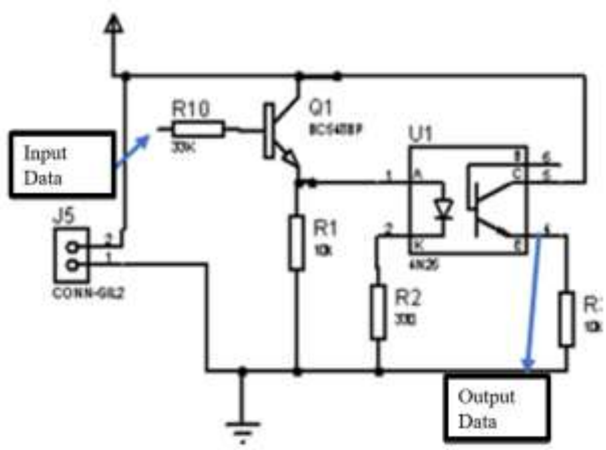

Figure 4 Isolation circuit
Source: Self Made

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4.-Power electronics

Once that the isolation circuit was performed the L298 module was used to control the power applied to the actuators, in this case, Peltier cells were utilized to control the interior of the measurement chamber.

5.-Measurement Chamber

A measurement chamber was designed to be capable to control the temperature of the QCM sensor. The CATIA 3D CAD (E. Torrecilla (2013), software was used to develop a model. Built it from steel in a nonagonal shape prism (Figure 5), with external dimensions of (ø:106 mm, H:200 mm) and internal dimensions of (ø:101.6 mm).

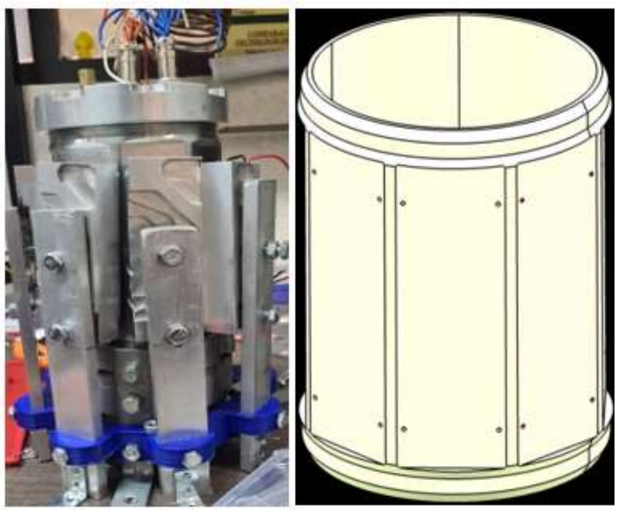

Figure 5 Measurement Chamber
Source: Self Made

A cover (ø:110mm, H:20mm) was designed with connectors for the temperature and QCM sensors that will be placed inside the camera. In addition, some arms are built, which are manufactured using steel in a CNC machine. Moreover, a support (Figure 6) is designed for the arms that hold the heatsinks and Peltier cells, the support was manufactured using ABS material to be printed on a 3D printer.

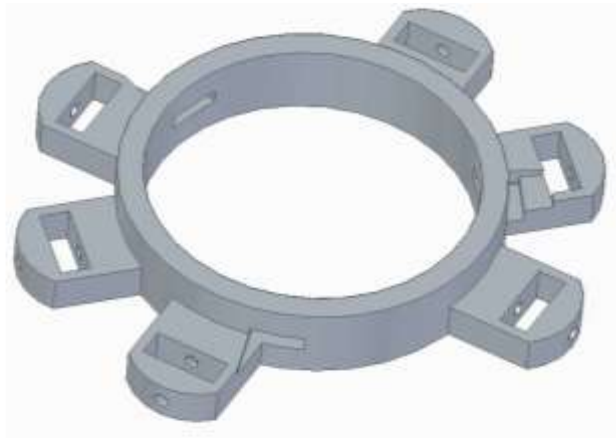

Figure 6 Arms support CAD
Source: Self Made

Experimental Results

In order to verify the correct operation of the system, QCM gas sensors with AT cut were built applying a sensing film of ethyl cellulose using the casting method. The crystal used for this experiment has a resonance frequency of approximately 12 MHz. Once the sensing film was applied, a frequency shift of ΔF = 4.39 KHz was obtained, which implies a thickness of the sensing film of 0.11 μm. Figure 7 shows the impedance curve obtained from the sensor developed.

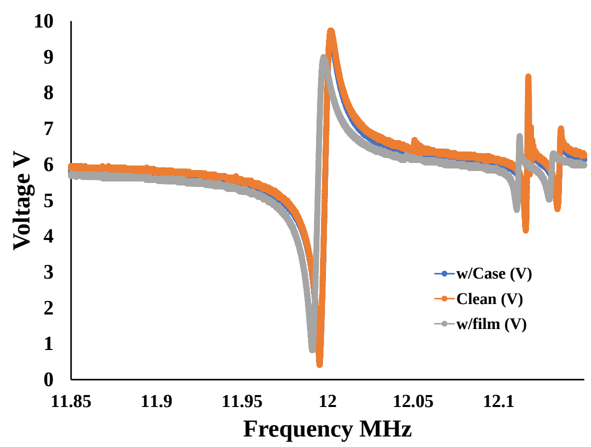

Figure 7 Impedance curves for a 12 MHz crystal with case, without case, and with sensing film.
Source: Self Made

Such plot shows the resonant frequency peak for each stage of the construction of the sensor, as can be observed, the sensor has proper performance.

Subsequently, once the sensor was ready and tested, the sensor response measurement stage was added, obtaining a complementary experimental arrangement, as shown in Figure 8.

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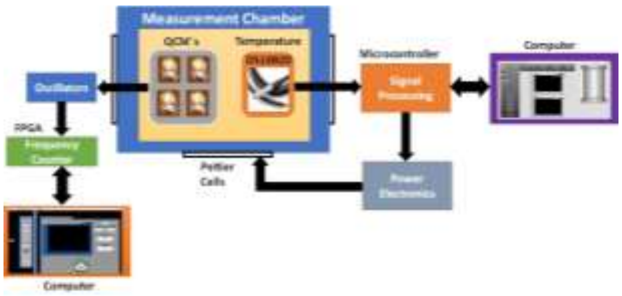

Figure 8 Complementary Experimental setup.
Source: Self Made

It can be observed an oscillator was added to excite the sensor using the piezoelectric principle to obtain the frequency response of the QCM sensor. A frequency counter is used to measure the sensor response (Muñoz Mata, *et al* 2012), with a resolution oh 1 Hz. Finally, the data are sent to the computer to visualize and store the sensor response information.

For the purpose of proving the effectiveness of the temperature regulation system developed, first, an open loop test was performed in order to obtain the resolution and range of the temperature of the implemented system. We could observe that the system heats at a rate of approximately 2°C/min over a range of 15°C to 50°C, and cools at a rate of approximately 0.8°C/min over a range of 50°C to 25°C, considering that the previous system achieved a heating time of approximately 0.9°C/min, with these results we achieve a significant improvement. Figure 9 shows the response ramp of one of the experimental tests performed.

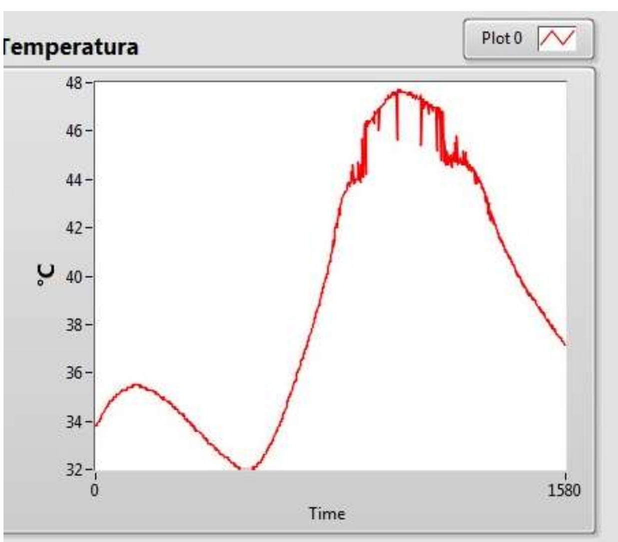

Figure 9 Response of the system in open loop
Source: Self Made

Figure 10 shows the temperature curve within the system using a PID controller (Hernández-Guzmán *et al* 2013), where the desired temperature i set at 30 °C. There is a closed-loop error range of approximately ± 1°C, with a proportional gain kp= 5 and an integral time constant Ti: 0.001. In this case, a derivative time constant was not used, since experiments are still being performed to optimize the controller.

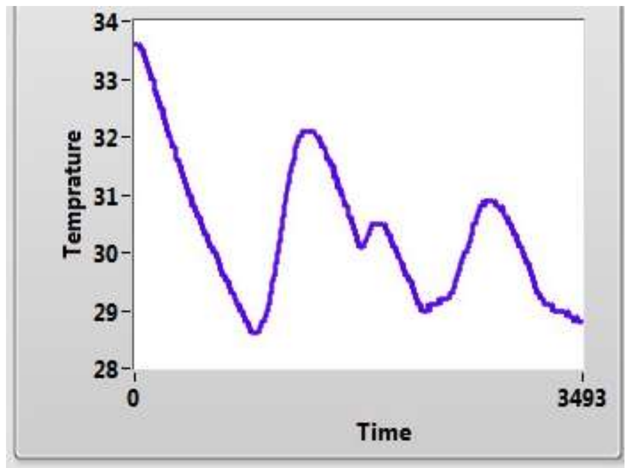

Figure 10 System response using a PID controller for a setpoint of 30 °C
Source: Self Made

Furthermore, the temperature was set at 25 °C, 35 °C and 45°C approximately. Experiments were performed, which consist in to measure the response of the gas sensor previously developed at three different temperatures.

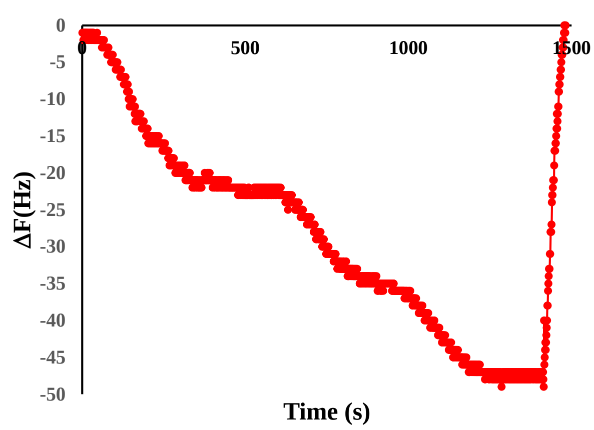

Figure 11 QCM gas sensor response at 25°C.
Source: Self Made

Once the temperature gradient is achieved at 25 °C, the frequency counter was started to measure the sensor response, applying 15500 pm of ethanol samples.

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In Figure 11 is shown the obtained response of the QCM sensor. As can be observed, the frequency shift for the first sample injection was of ΔF=22 Hz in 600 seconds approximately. When we applied the second sample a frequency shift of ΔF=37 Hz in 1150 seconds. For the third sample injection shows a ΔF=49 Hz in 1550 second approximately.

Figure 12 shows the obtained results of the sensor for a temperature inside the chamber of 35 °C, where significant differences can be appreciated.

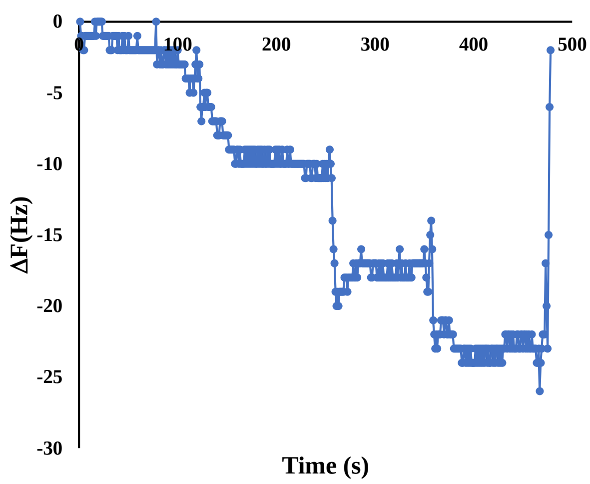

Figure 12 QCM Sensor response at 35 °C.
Source: Self Made

As the previous experiment, three ethanol samples were applied with the same ppm concentration. As can be observed, for the first sample injection, a frequency shift of ΔF=12 Hz in approximately 200 second was obtained. For the second sample was obtained a response of a frequency shift of ΔF=20 Hz in 390 second. When a third ethanol sample was injected, a shift of ΔF=25 Hz in a time of 550 seconds was obtained. As can be appreciated, when the temperature step is increased produces a shift in the base response of the sensor. Hence, if the temperature set increases the sensor base response decrements, due to the temperature effect in the measurement chamber, as well as the response time.

Finally, a third test was performed, the temperature was set at 45 °C, which experimental results can be observed in Figure 13. A frequency shift of ΔF=9 Hz was obtained after a first ethanol sample was applied. For the second sample a response of ΔF=17 Hz and ΔF=22 Hz for the third sample.

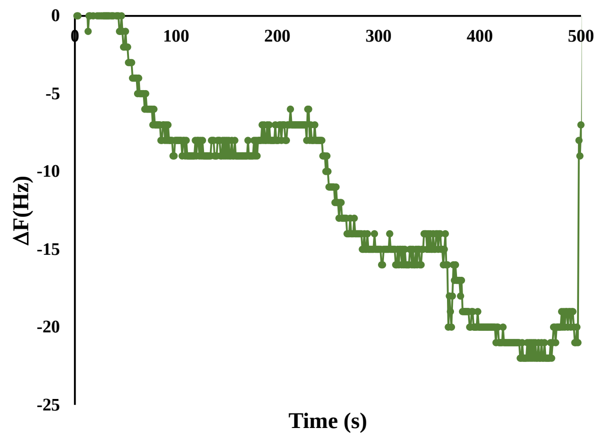

Figure 13 QCM sensor response at 45°C
Source: Self Made

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In order to be able to appreciate the effects of the temperature of the measurement chamber for this type of QCM sensors, all the raw responses were plotted. As can be observed in Figure 14, there is a change in the frequency base-line of the sensor for each configured temperature step, which corroborates the fact that this type of QCM sensors is sensitive to changes of temperature.

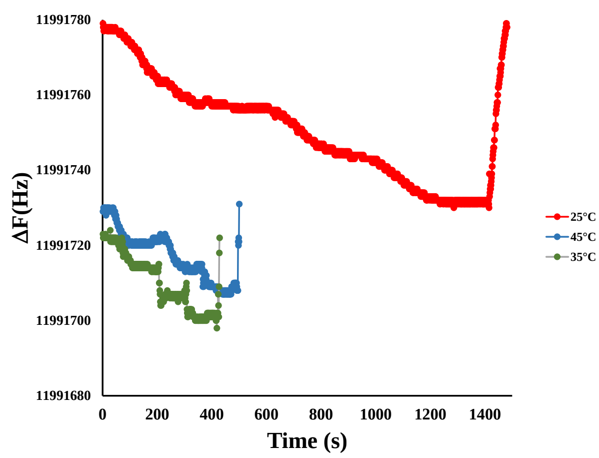

Figure 14 Raw response of the QCM sensors for different exposition of temperature
Source: Self Made

In addition, linear adjustments of the sensor response are obtained as a function of the applied concentration, as can be appreciate in Figure 15 for the response of the sensor exposed to a temperature of 25 °C, there is a correlation coefficient of R^2=0.9891.

ISSN 2523-0344

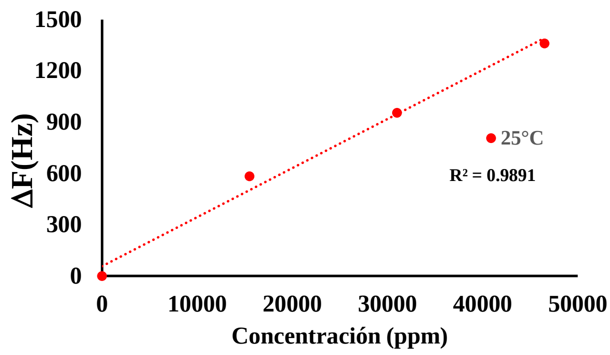

Figure 15 Linear adjustment of the frequency shift as a function of the concentration (correlation coefficient R^2) at 25 °C
Source: Self Made

For the case of the sensor response at a temperature of 35 °C we obtain a coefficient of R^2=0.9934, and for a applied temperature of 45 °C a correlation coefficient was achieved of R^2=0.9914 as observed in Figure 16.

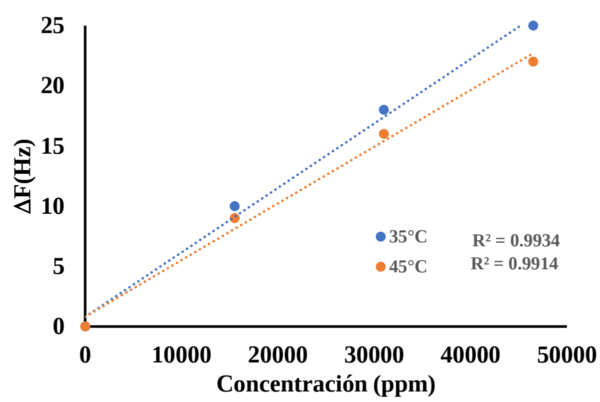

Figure 16 Linear adjustment of the frequency shift as a function of the concentration (correlation coefficient R^2) for 35 °C and 45 °C
Source: Self Made

As it could be observed, it had been obtained responses from real QCM sensors, such responses correspond to typical curves characteristics for sensors exposed at different temperatures, which indicates that the implemented system, at least preliminary, has a satisfactory performance.

Acknowledgments

To the Universidad Tecnológica de Puebla for the opportunity in the use of the facilities for the development of this project.

Conclusions

A preliminary system for the update of a quartz crystal gas sensor response measurement system has been developed, obtaining typical responses from QCM sensors exposed at different temperatures.

It is important to mention that the temperatures of the interior of the measurement chamber are reached in an approximate time of 10 minutes for 25°C, 16 minutes to reach 35°C and a time of 23 minutes for 50°C. In addition, after performing the experimental tests. we realized that the actuators (Peltiers) were not working properly, therefore, solving this issue, the system performance could be improved significantly.

The measurement chamber presents improvements with the reduction in thickness from 8 mm to 4.4 mm, thus, helping to distribute the temperature evenly inside the chamber. In addition, to being able to place more actuators in the system due to the design of the walls.

Future work

It is intended to improve the cooling speed, as well as the control algorithm of the control operation of the chamber. Sensors will be added to measure and control humidity inside the chamber. Moreover, temperature sensors will be placed on the base and the upper part of the chamber in order to collect more accurate information of the behavior of the temperature. In addition, it is planned to change the digital sensors to analog to improve accuracy.

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ISSN 2523-0344