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Development of a portable gas sensing platform with QCM sensors for volatiles of agro products

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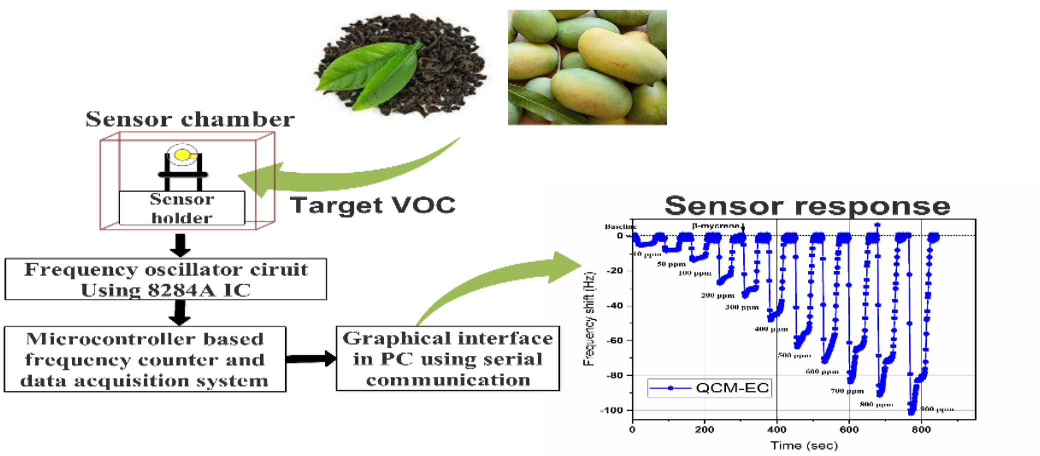
Article



Abstract

An approach towards developing a portable electronic nose with a quartz crystal microbalance sensor (QCM) is described in this paper. The developed portable system comprised of a QCM sensor chamber, electronic circuits for frequency oscillation, Arduino Due development board, a USB based 32-bit microcontroller system comprising of ARM-M3 SAM3X8E chip for data processing and data acquisition, followed by an SD card slot for data storage and a liquid crystal display (LCD) for display. The system can be operated with 5V using a commercial power bank. The real-time data can also be viewed as graphs on a PC or laptop using serial port communication. This paper demonstrates the instrument and works to detect different VOCs present in fruits and spices effectively using coated QCM sensors. The performances of the developed system have been evaluated by determining the sensitivity of maltodextrin (QCM-MDEX) and ethyl cellulose (QCM-EC) coated sensors for determining methyl salicylate and β-myrcene, respectively. The system showed satisfactory sensitivity with fewer errors. Therefore, the system can be a low-cost, robust, and user-friendly solution for aroma-based quality analysis in the agro-industry.

Keywords: Portable sensing system, Embedded system, Quartz crystal microbalance

Introduction

Olfaction is one of the most important attributes of the human sensing system used to differentiate materials based on their aroma. A major advancement and research are being carried out during the last few decades targeting to develop devices that can mimic the core functionality of the human nose to detect aroma.[1,2] Currently, E-noses are used extensively in various applications that include healthcare,[3,4] agriculture,[5] quality control of food products,[6–8] indoor air quality, defense sector, and estimation of poisonous and inflammable gases.[9–11] However, some commercial E-noses are available but they are too costly and require a computer or laptop for its data processing as well as data acquisition. Hence the system is not suitable for portability.

The advent of embedded technology paved the way for the development of low-cost and power-efficient devices and created an opportunity to replace the need for bulky and power-consuming PC for storage and data processing. Some research findings were also reported in various peer-reviewed journals that describe the development of portable E-nose using microcontrollers that are low-cost and compact.[12–15] In all the commercial e-nose systems, metal oxide semiconductor (MOS) based gas sensors are extensively used.[16–18] However, MOS sensors have various disadvantages since it is very difficult to

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fabricate MOS, and thus to achieve a selective metal oxide gas sensor in practice is very low.[19] The developed system is intended for the detection of a specific VOC present in any aroma employing an aroma-specific coated quartz crystal microbalance (QCM) sensor.

The QCM sensor consists of a quartz crystal sandwiched between two gold/silver electrodes. The oscillation of the QCM sensor and the temperature behavior depends on the cutting angle of the crystal substrate concerning the main crystallographic axis. When AC voltage is applied, the two faces oscillate against each other. At resonance, a wavelength of AC voltage exactly matches the plate thickness. The QCM sensors can be tailor-made for detecting specific volatile organic compounds (VOC) upon coating it with specific adsorbing coating materials.[5,20] QCM sensors have been implemented for VOC detection of various agricultural products.[21–25] During the sensing process, the change in resonant frequency (Δf) due to change in mass upon adsorption of VOC on the crystal surface is considered for sensitivity calculation. For small and rigid mass loadings on QCM, the shift in resonant frequency (Δf) is according to Sauerbrey's equation[26] given by

$$\Delta f = \frac{-2 f_o^2 \Delta m}{A\sqrt{\rho_q * \mu q}} \quad (1)$$

Where f_o is the fundamental resonance frequency, Δm is the mass deposited on the QCM surface, A is the active electrode area, ρ_q is the density of the crystal, μ_q is the shear modulus of the cut face of the crystal. For small mass loading Δm, the shift in resonant frequency Δf holds a linear relationship, and hence QCM sensor acts as a sensitive microbalance to detect small masses adsorbed on it [27].

The present study focused on the development of a low-cost portable VOC detection system using the Arduino Due development board for data processing and data acquisition. The system is also equipped with an LCD Display for data output and an SD card for corresponding data storage. The working of the system was validated by evaluating the sensitivity of two fabricated sensors reported in the previous literatures.[28,29]

System Overview

Basic block diagram of the developed system

The working module typically consists of a sample delivery system, a detection system, a hardware module, and a software module. The sample delivery system generates the headspace (volatile compounds) of a sample. This headspace is injected into the sensor array of the electronic nose instrument. The sample delivery system maintains constant operating conditions. The detection system consists of a QCM sensor, that experiences a change of electrical properties, in contact with volatile compounds. The hardware module is responsible for all the necessary circuits for the power supply for the QCM oscillator, microcontroller units. The software module controls the operation of the hardware interface, along with the processing and storage of data. The data acquisition unit comprising Arduino Due development board controls the voltages for the operation of the delivery valves for sampling and purging phases and saves the frequency output from the sensor. The functional block diagram of the developed sensing system is shown in figure 1.

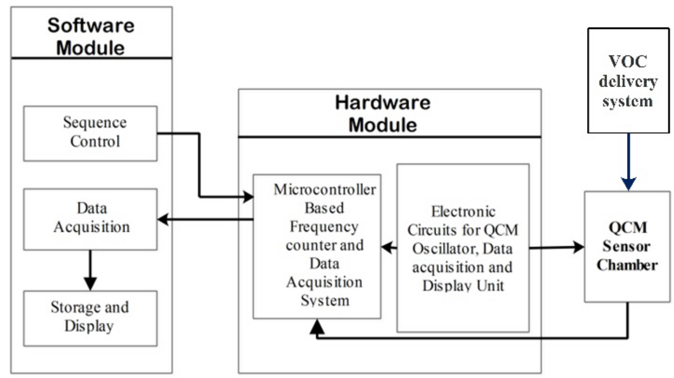

Figure 1. Block Diagram of the developed sensing system

Development of the sensing system

The coated QCM sensor is placed in a small sensor chamber which is attached to a suction pump for purging ambient air through a three-way selector valve into the sensor chamber. The sensor chamber is an airtight container made of Teflon. The top cover can be easily removed to install the QCM sensor for sniffing applications. The volatile organic compounds are delivered through the VOC inlet into the sensor chamber. The oscillation frequencies of the QCM sensor are generated by 8284A IC which is a high-performance CMOS clock generator-driver.

The development of the frequency counter has been carried out using Arduino Due development board (Arduino SRL, Strambiano, Italy) which hosts an Atmel SAM3X8E chip that includes ARM Cortex M3 core running up to 84 Mhz. It includes 256-512 KB FLASH, 32-100 KB SRAM, and lots of interfaces: CAN, SPI, I2C, ADC, DAC, PWM among others. The microcontroller contains a 32-bit timer counter with an adaptable microcontroller timer clock up to 42 MHz, making it suitable for calculating frequency up to 21 Mhz. Thus, 10 MHz QCM resonant frequency can be suitably measured using this system.[7]

The frequency of 10 MHz QCM obtained from the oscillator circuit was delivered to the counter module of the Arduino Due consisting of nine timer/counter channels (TCLK0 – TCLK8). The counter channel 8 (TCLK8) is used to generate a gate time of 1 sec, whereas the input signal is provided at TCLK0 (Digital pin 22) which measured the number of rising edges of the signal. When the gate interval time exceeds the frequency measurement was calculated by the total number of rising edges calculated within that time frame.

Data Acquisition and display unit

The frequency generated by the counter module can be stored in real-time using a micro-SD card (on a Catalex breakout board) and send the same data over Serial to the PC. The micro-SD card supports SPI communication pins to receive data from the microcontroller. The MISO, MOSI pins are connected to digital pins 12 and 11 respectively. The CS (Chip Select) is set at pin 10 and CLK is assigned to pin 14 of the microcontrollers.

A 20×4 LCD is used for displaying the sensor values and works on a 5V power supply from the Arduino Due development board. The microcontroller board uses 6 digital pins for the proper functioning of the LCD. The LCD registers from D4 to D7 are connected to the microcontroller's digital pins from 2 to 5. The Enable pin is be connected to PIN 7 and the RS (Register Select) pin is be connected to PIN 1. The R/W (Read/Write) pin is connected to the ground and the V_o pin is connected to the potentiometer for contrast adjustment. The complete pin diagram is shown in figure 2.

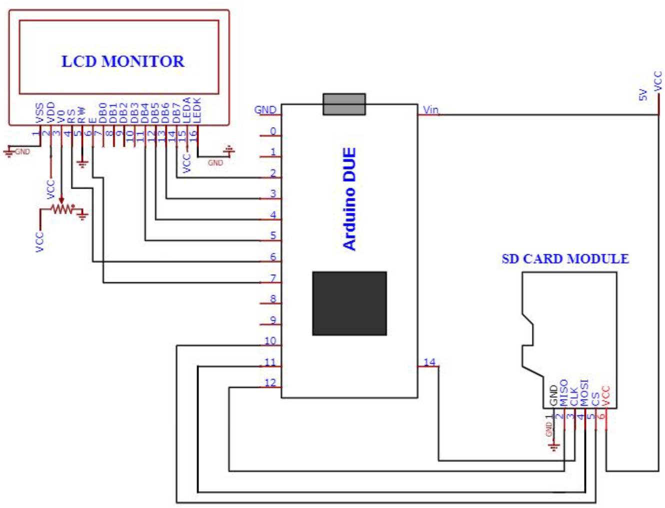

Figure 2. The pin diagram of data storage and display unit

VOC DETECTION USING THE QCM SENSING INTERFACE

The developed system has been utilized for the study of VOCs of two agro products like tea, and mango. Two VOCs namely methyl salicylate present in black tea [28] and β-myrcene present in mango [29] have been considered for evaluating the sensor response in this study.

Materials

10 MHz QCM sensor having 8 mm diameter AT-cut quartz crystal with silver electrodes were procured from Andhra Electronics, India. The adsorbing materials for the study Maltodextrin and Ethyl cellulose were purchased from Merck Specialities Pvt. Ltd, Mumbai. Additionally, the test volatiles namely methyl salicylate and β-myrcene were purchased from Sigma-Aldrich, Germany. The chemicals were used unaltered as received.

Sensor fabrication

As discussed in the previous works[28,29] the development of the sensors was followed using the nebulization technique. Proper coating with maltodextrin and ethyl cellulose resulted in the fabrication of QCM-MDEX and QCM-EC sensors respectively. The study of the sensitivity of the developed sensor has been performed by injecting methyl salicylate and β-myrcene within the range of 10-900 ppm into the sensing system. The sensitivity of the sensors was measured for determining the accuracy obtained with the developed system.

EXPERIMENTAL

Experimental setup and working modes

The developed sensing interface generally operates in three modes i.e., pre-testing stage, sampling stage, and purging stage. In the pre-testing stage, the system generates a new .csv file in the SD card and continuously takes sensor input waiting for the sensor stabilization.

The saturated concentration of the volatiles was prepared in a 10 for injection into the sample chamber. The VOCs were then injected varying between 10-900 ppm using a glass syringe [30] for evaluation of the sensitivity of the sensor using the developed system.

During the sampling stage when the VOC has injected into the sensor chamber the last frequency of the pre-testing stage was being recorded and it acts as the initial frequency of the sensor. The continuous frequency change is being monitored and the real-time frequency deviations are displayed on the LCD and consecutively stored in the SD card. The real-time slope of the curve is also being monitored per second using the following equation:

Slope = (Present Frequency – Previous Frequency) / 2

If the slope ranges between 0 and 1 the sensor output tends to attain the steady-state. The sampling stage was continued for 25 secs to attain the saturated state of the sensor before purging. During the purging stage, the system displays the final deviation of the sensor and waits for the next pre-testing stage. A control button has been implemented for the initiation of the different stages of the system. The real-time monitoring and storage of data into the PC can be established by serial communication with the Arduino Due board and using PLXDAQ software for data storage. The software module has been developed in a C/C++ environment which provides low cost and highly productive programming for the peripherals. The complete sensing setup has been shown in figure 3.

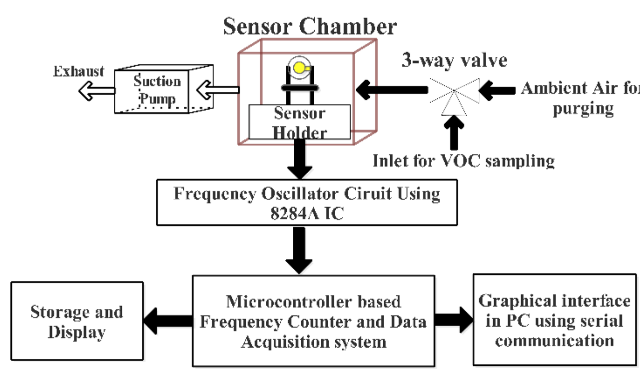

Figure 3. The schematic of the QCM sensor-based sensing system.

RESULT AND DISCUSSION

Case study 1: Detection of Methyl salicylate VOC

The fabricated QCM-MDEX sensor was tested with 10-900 ppm of methyl salicylate for the detection of its sensitivity. The QCM-MDEX sensor upon injection of methyl salicylate showed frequency changes (Δf) from its resonance condition. The frequency changes due to adsorption of volatile have been successfully stored in the SD-card module. The sensor response curve at different concentrations has been depicted in figure 4.

The sensitivity of the QCM-MDEX sensor obtained upon controlled exposure to methyl salicylate gas results in 0.1166 Hz/ppm with linearity having R^2 value of 0.9972. The electronic system provides very linear and accurate sensor readings for all the VOCs in the range of 10 to 900 ppm when injected into the sensor chamber.

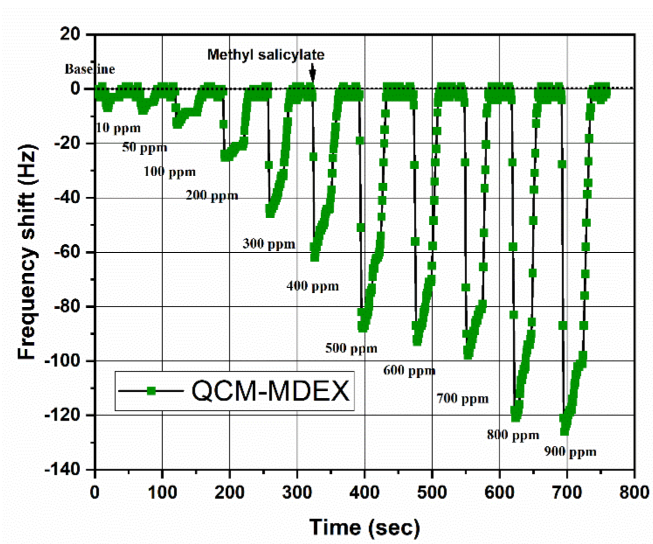

Figure 4. Maltodrextrin coated QCM (QCM-MDEX) sensor response

The developed interface provides a quick response during the sampling process and its data acquisition upon input of different concentrations of methyl salicylate monitored thrice. The sensitivity plot of the MDEX-QCM sensor has been depicted in figure 5.

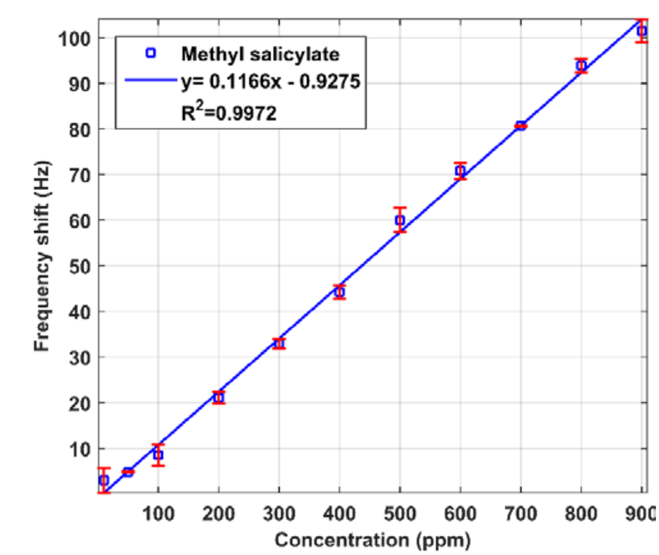

Figure 5. Sensitivity plot of maltodrextrin coated QCM (QCM-MDEX) sensor

The error percentage of the obtained sensitivity of the MDEX-QCM sensor as studied in previous work [28] was calculated to be 2.34%.

Case study 2: Detection of β-myrcene VOC

In this study, the developed QCM-EC sensor was tested for its sensitivity towards β-myrcene VOC present in mango. The experimental procedures were maintained similar to the previous case study discussed above. The sensor showed prompt response upon injection of the generated 10-900 ppm of the volatile. The sensitivity plot as depicted in Fig. 6 explains the sensitivity to be 0.111 Hz/ppm. The linear curve fitting of the obtained data showed R^2 value of 0.9965.

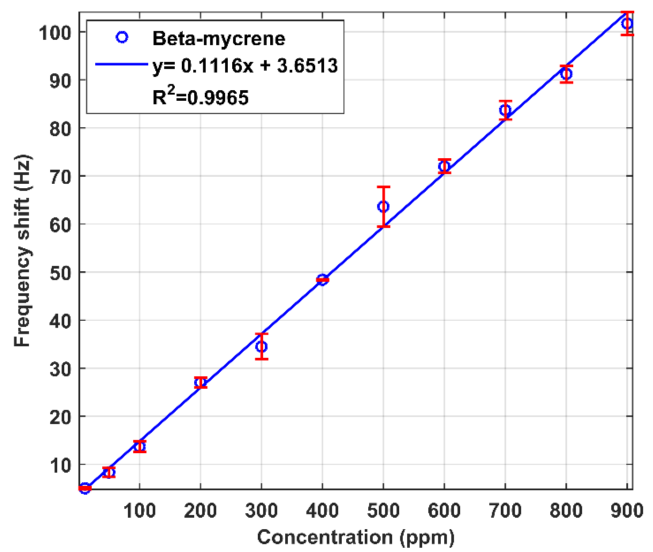

Figure 6. Sensitivity plot of ethyl cellulose coated QCM (QCM-EC) sensor

Moreover, the error percentage of the sensitivity obtained in this developed system was found to be 11% as reported in earlier work [29]. The sensor responses observed in this study showed similar responses as the reported data as shown in figure 7.

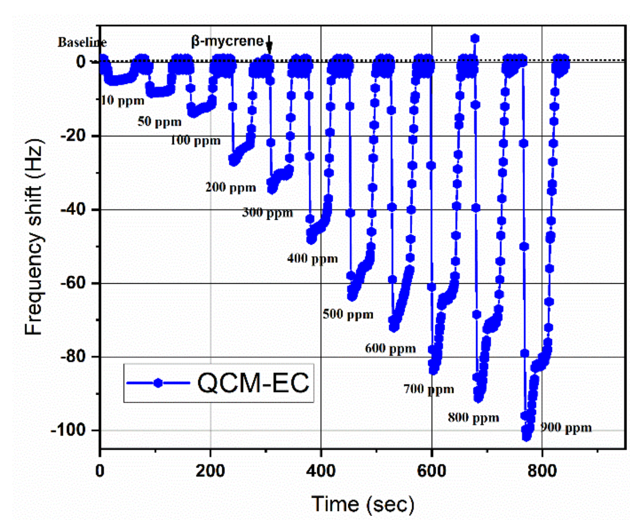

Figure 7. Ethyl cellulose coated QCM (QCM-EC) sensor response

The studies conducted with the developed portable interface provided a low-cost and efficient alternative for the detection of volatiles using the QCM sensor platform. However, the system can be made viable for a wide range of volatiles depending on the proper fabrication of the QCM sensor based on the appropriate coating material.

Conclusion

The studies conducted with the developed portable interface provided a low-cost, fast and efficient alternative for the detection of volatiles using the QCM sensor platform. However, the system can be made viable for a wide range of volatiles depending on the proper fabrication of the QCM sensor based on the appropriate coating material. The microcontroller-based gas sensing platform developed in this work provides a good solution for portability as well as power usage. The present work describes the development of two important gas sensors for detecting the VOC of tea and mango namely methyl salicylate and β-myrcene. The developed sensors were tested with the respective volatiles using the developed system. The result showed identical results as obtained from the previous studies. However, the error percentages of QCM-MDEX and QCM-EC were found to be 2.34% and 11% respectively. The sensitivity study was performed for the two developed sensors. The data can be accurately stored in the SD-card to analyze the sensor performance for varying concentrations. Thus, further studies can be performed for determining the other sensor characteristics like selectivity, repeatability easily using this device. Thus, the portable electronic nose using the QCM sensor discussed in this work can be beneficial for determining the VOCs in different agro-industries.

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