A New QCM Based E-NOSE Model Using Decay Method

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Abstract: - In this paper we present the possibility of developing an Electronic - Natural Olfactory Sensors Emulator (E-NOSE) based on an array of Quartz Crystal Microbalance (QCM) sensors exploiting the advantages of using decay methods for analyzing the QCM sensor (QCMS) responses. The usage of smart coating implies the necessity of monitoring extra parameters besides the usual oscillation frequency variation in QCM sensing applications. A proposed E-NOSE model using QCM decay method for studying the sensor array responses is presented.

Key-Words: E-NOSE, QCM, sensor array, quartz crystal microbalance, thickness share mode, bulk acoustic wave, pattern recognition.

1 Introduction

The human nose has been used as an analytical tool in many industries to measure the quality of food, drinks, perfumes and also cosmetic and chemical products. The sense of smell varies from one person to other and the accuracy may be affected by physical and mental health as well as fatigue. In order to eliminate these, research has developed various methods of replacing the biological nose. A cost effective concept are E-NOSE systems, which are designed to mimic the mammalian olfactory sense.

In the last few years more and more attention is given to sensing applications for environmental, medical, biotechnological and biochemistry fields. Governments are paying a lot of attention to security at their borders and invest money in systems that can prevent a catastrophe, saving in this way a lot of lives and property values.

Since the introduction of “smart coatings” for piezoelectric sensors new opportunities have opened. E-NOSE devices using such QCM sensors represent a hot area in research.

2 Theory

In this section the accent is on the QCM functionality in gaseous medium and its utilization in E-NOSE devices. This is a very useful overview for the new researchers in the field because it presents the essentials of the QCM utilization in sensing applications from electrical point of view.

The piezoelectric phenomenon is very complex and covers concepts of electronics as well as areas of classical physics, acoustics, wave’s propagation, electrostatics, fluids dynamics, crystallography etc., and only a few disciplines of science need to be so familiar to so many fields of physics.

2.1 The QCM Sensor

A QCM or thickness shear mode device is a piezoelectric bulk acoustic wave resonator which is excited by an alternating voltage.

It was first introduced by Sauerbrey in 1959 [1]. He showed that the resonant frequency shift of the QCM is related to changes in mass at the crystal surface by the equation:

$$\Delta f = \frac{-2 f_0^2 M_f}{A\sqrt{\rho_q \mu_q}} = -C_f \, \Delta m \qquad (1)$$

where: Δf is the change in resonant frequency, f_0 is the resonant frequency, M_f is the mass change, A is the electrode area, ρ_q is the density of quartz and μ_q is the shear modulus, Δm is the change in mass per unit area, C_f is the sensitivity factor for the crystal.

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The QCMS (Fig.1) is usually an AT-cut quartz crystal sandwiched between two metal electrodes, one of the electrodes is coated with a sensitive material which changes its mass due to analyte adsorption, causing a change in resonant frequency.

QCMS have gain considerable interest due to their high sensitivity, simplicity, low cost, real-time monitoring, and for the advantage given by the diversity of sensitive coatings [2], [3].

The high mass sensitivity of the QCM is explained by the very high intensity of the time-dependent inertial field, acting on the deposited film at the surface of the quartz resonator [4]. Another great benefit of the QCMS is that their operation is gravity independent so they can be successfully used in space exploration research [3].

The QCMS's have also a wide range of applications in areas of food, environmental and clinical analyses. More recent developments have focused over developing electrode surface chemistry (i.e. specialized polymer coatings) so that these devices can be applied as discriminating mass detectors for specific gas detection, bio-sensing and surface-molecule interaction studies [2], [5].

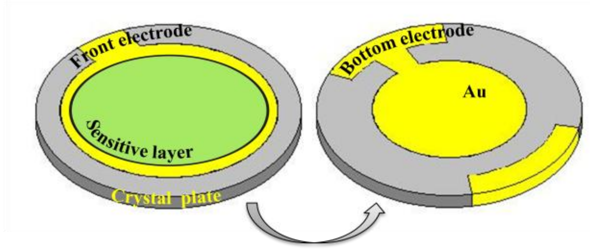

Fig.1 Front and bottom electrodes of a QCMS

2.1.1 QCMS Theoretical Background

The Sauerbrey equation, (1), is only applicable to uniform, rigid, thin-film layers [1]. Depositions which fail to fulfill any of these conditions exhibit more complicated frequency-mass correlations.

It is generally accepted that the Sauerbrey equation can be used for accurate results when if the resonance frequency shift caused by the mass loading is less than 2% of the frequency of the unloaded crystal.

Behrndt modified the Sauerbrey equation, taking into account the frequency f_c of the coated quartz resonator, and proposed the following frequency-mass relationship which is accurate for frequency shifts up to 10% [6]:

$$\Delta f = \frac{-f_q f_c M_f}{A\sqrt{\rho_q \mu_q}} \tag{2}$$

Lu and Lewis included the acoustic properties of the deposited film. The dependence of Δf on Δm, which is currently applied by most QCM in gas phase depositions, it is called "Z-match method":

$$M = \frac{arctan\, Z\, tan\, \pi F}{\pi Z(1-F)} \tag{3}$$

Where: $Z = z_q/z_f = \rho_q \mu_q/\rho_f\, \mu_f$ is the ratio of the acoustic impedances, $M = \rho_f l_f/\rho_q l_q$ is the ratio of areal densities, $F = (f_q - f_c)/f_q = -\Delta f/f_q$ the normalized frequency shift, l_f is the deposited film thickness [7]. This is well supported by the experimental data for frequency shifts up to 35% of the uncoated quartz crystal [6].

Under liquid loading an additional frequency shift arises, which is proportional to the liquid density and viscosity. The frequency change, when one face of a quartz crystal resonator is in contact with a liquid was calculated by Kanazawa [8]. The model holds as long as the film is assumed to be thin and rigid. For when viscoelastic proprieties of the load must be considered more complex theories been developed by Mecea [6], Voinova [9], Johannsmann [10].

2.1.2 QCM Electrical Model

In order to treat the sensor as a component included in electronic circuits it is useful to have an electrical model.

The loaded quartz is usually described by Butterworth Van Dyke (BVD) equivalent circuit (Fig.2), which is an approximation of the full electrical equivalent, so-called Transmission Line Model, assuming that the resonator operates around the motional series resonant frequency (MSRF) [2].

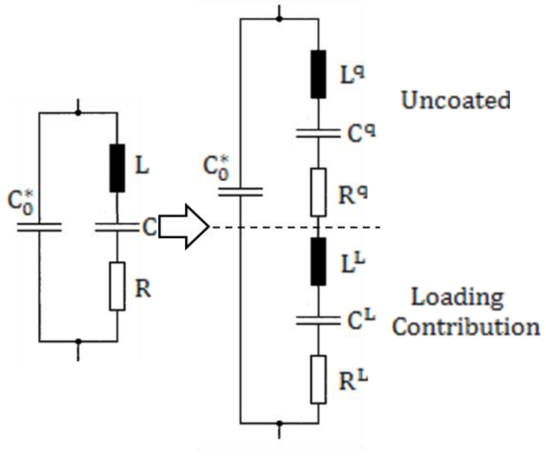

Fig.2 a) BVD model b) Extended BVD model

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BVD circuit consists of two parallel branches: the so called “motional arm”, which models the motional physical phenomenon, and the static arm formed by a capacitor which models electrical capacitance arising from the dielectric material placed between the two electrodes and the parasitic capacitances external to the resonator. Each of the circuit elements of the extended BVD can be related to the physical properties of the quartz and the load.

The most significant parameter of the model is the MSRF, which is defined as the frequency at which the motional reactance vanishes:

$$f_s = \frac{1}{2\pi\sqrt{LC}} \tag{2}$$

MSRF is sensitive to changes in both L^L and C^L, i.e. mass displaced during vibration and elasticity, but is independent of parallel capacitance changes.

Changes in the loading can also reflect on the motional resistance R^L , which is a measure for dissipation of the oscillation energy induced by viscosity of the surrounding medium and which doesn’t produce changes in the MSRF. Sometimes both parameters, MSRF and R, are necessary for a correct characterization of the addlayer [11].

2.1.3 Decay Method

The three most common methods for studying QCMS responses are: a) using the sensor as the active element in an electronic oscillator, b) recording the changes in spectral behavior, and c) examining the transient decay of the initial excitation signal.

In this last technique the piezoelectric resonator is excited to the MSRF or parallel resonant frequency. After excitation the signal decays as an exponentially damped sinusoidal signal (3), as shown in Fig.3:

$$U(t) = A_0 e^{-t/\tau} \sin(2\pi f t + \varphi) \tag{3}$$

Where: A_0 is the undamped amplitude (t = 0), φ is the phase, τ the decay time constant and f is the resonant frequency.

From the decaying signal, it’s possible to determine the resonant frequency and the decay time constant, which is related to Q-factor or dissipation (D) by (4). The motional resistance R, the Q-factor or D are a measure for the acoustic energy dissipation in the coating while the frequency shift is related to acoustic energy storage.

$$Q = \pi f \tau = \frac{2\pi\, E_{storred}}{E_{dissipated}} = \frac{1}{D} \tag{4}$$

Schematics of the circuits used in decay method analyses are presented by Rodahl et all [12].

This method facilitates the opportunity to excite the sensors at multiple harmonic frequencies. This is extremely valuable in data analysis, particularly when studying viscoelastic loads [13].

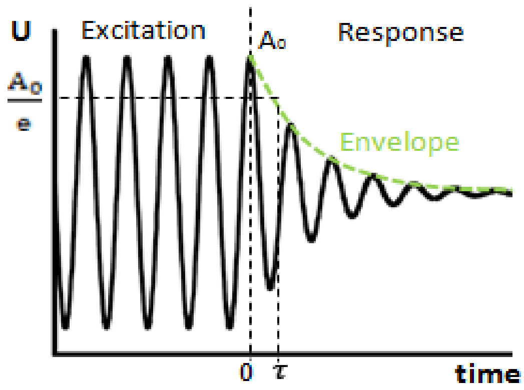

Fig.3 Excitation signal and the QCM response

Recently, the decay method was introduced with two simultaneous excitation frequencies from the harmonics of the resonance frequency. One of the harmonics is used for evaluation of the frequency shift and dissipation, while the other harmonic is used for perturbation purposes by changing the driving amplitude [14].

The decay method also reduces the cost and size of the instrumentation in comparison with network or impedance analysis and gives several advantages over the utilization of QCM in oscillator circuits [11].

2.1.4 QCM Gas Sensor Arrays

The sensitive layer (i.e. polymer layer) deposited on the quartz plate collects the odorants onto the sensor surface. The adsorbed molecules are detected by the changes in the propagation of the acoustic wave caused by the added mass and viscoelastic effects on the surface layer.

The sensor responds to the analyte molecules in the sorbent phase and not in the gas phase and it is necessary to calibrate the sensor for quantitative analyses trough the partition coefficient [2]:

$$K = \frac{c_s}{c_v} \tag{5}$$

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Where: c_s is the analyte concentration in the surface sensing layer and c_v represents the concentration in the gas.

Sensors arrays are used for applications when complex gas mixtures are analyzed. The sensors are carefully chosen regarding the application specific.

The majority of reported QCM sensor arrays where based on combinations of single QCM sensors coated with different sensitive layers [15]. In recent years, from the desire of reducing arrays dimensions and eliminating significant variation in sensing responses of identical sensors due to fabrication process and environmental influences, single plate QCM arrays have been developed [16], [17], [18]. In such a device, n couples of electrodes (n channels) are deposited on a single quartz plate in such way to limit the interfering between the channels [17].

2.2 The E-NOSE

The E-NOSE is an electronic device capable of detecting and recognizing complex odors. Those devices find their applicability in a variety of areas such as: food industry, medicine, safety, perfumes industry, space exploration etc. [19-21].

Typically, it consists of an array of gas sensors with different selectivity, electronic circuits for signal conditioning and data analyses. For data analyses Artificial Neural Networks (ANN) and Fuzzy Systems are desirable because of their bio-inspired nature. Array responses are subjected to feature extraction and pattern recognition algorithms. Other usual requirements for a commercial E-NOSE are: portability which comes in hand with low power consumption, flexibility, low cost and easy to use.

Being a relatively new area of research, it currently has a high potential both in building new applications and in improving the existing ones [19].

2.2.1 QCM Based E-NOSE

QCMS are not that common comparing other type of sensors used in E-NOSE devices because of the extra electronic circuitry needed.

However, because of the unique particularities of QCMS, QCM based E-NOSE systems represent an area of interest in research, interest which materialized in some applications like: fish freshness monitoring [15], anesthetic dose level detection [20], characterization of plant degradation process [21] etc.

Most devices are designed for specific applications and in most cases the sensors where used as active element in an electronic oscillator. Though this is a suitable method regarding costs and power consumption, it drastically reduces flexibility of the device, because only one resonance frequency can be used, and a large array implies a high number of oscillators.

Some exceptions are reported in [22], [23] but the flexibility remains low in comparison with the method proposed in this paper.

3 The Proposed E-NOSE Design

Considering all aspects presented above one can see that, for a QCM based E-NOSE device, using decay methods is most suitable, especially when visco-elastic sensitive coatings (i.e. polymers) are used.

Development of a QCM based E-NOSE using decay methods brings a lot of challenges especially when regarding the requirements for commercial E-NOSE devices. In the development stage first step is to find a suitable programmable sinus generator to use as exciter for the sensors in array. For this application the generator must fulfill certain features like: frequency range to cover resonance frequency and few superior harmonics, fine resolution and fast frequency hopping. Such components are direct digital frequency synthesizers (DDFS) which can be found as integrated components (IC). They can provide up to 400 MHz sine wave signal, 32-48 bit tuning word, fast hopping and phase and amplitude control.

For better understanding of the concept a suggestive diagram of the idea is presented in Fig.4.

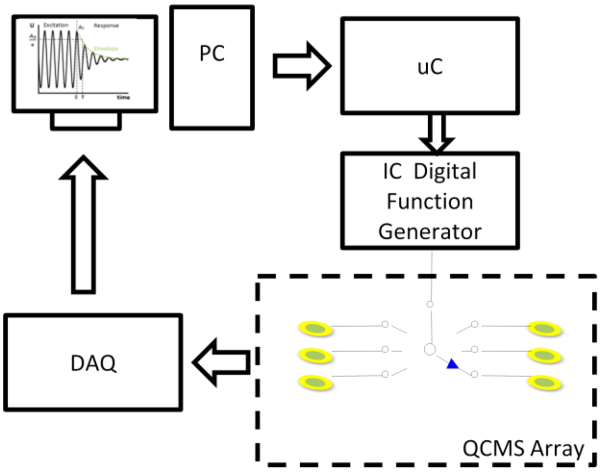

Fig.4. Block diagram of the QCM based E-NOSE

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3.1 The E-NOSE Algorithm
We assume that the sensors parameters are known from the manufacturer or from previously done measurements.

The µC is properly programmed for mastering whole assembly. After initialization, a tuning word is send to the digital sine wave generator (DSWG) and an excitation sinusoidal signal (f, A, φ) is generated for the first sensor. The sensor response after excitation is digitally acquisitioned trough the data acquisition system (DAQ). Next sensor is excited to its resonance and the algorithm is repeated until we have a complete array response.

The data analysis is made on the PC due to flexibility conferred by the specialized software, and for cost efficiency. From the digitized array responses Δf and ΔQ are extracted for each sensor, which means that for the entire array a 2 x N table is the response to given analytes, where N is the array dimension. The response is then subjected to a pattern recognition algorithm previously trained. ANN methods will be used exploiting their generalization power and bio-inspired nature.

Other option is to parallelize the excitation and the acquisition stage by using multichannel DSWG and DAQ. Instead of a specialized DAQ one can use a suitable digital oscilloscope.

Multiple odd superior harmonics excitation is also possible to implement if needed.

The design needs conditioning circuits after the sensor array. Some previously realizations can be found in [11], [12]. Depending on the chosen DSWG some filtering of generated excitation signal may be needed.

By using decay methods in a slow changing headspace user can reduce the power consumption by increasing the time between two consecutively measurements without affecting the accuracy of the measurements.

4 Conclusion
This paper is the result of a hard work informative research of the authors involving different areas of sciences which must converge in order to develop a modern analyzing tool. The accent was on the QCM operation in an array for odors sensing, but the paper is also useful to the E-Tongue developer since QCM's can operate in liquid medium under high damping conditions [2], [8].

The paper presents most important aspects of the theoretical background associated with the design of a QCM based E-NOSE device, and also indicates the most significant authors in the area.

The proposed E-NOSE design presents further research directions, and provides useful discussions on the concept revealing important features of such device. Benefits of such device are foreseen for many applications in which "smart" sensitive layers with viscoelastic proprieties are used.

Future research will be done in order to find most suitable interface and conditioning circuits and also developing a complex pattern recognition algorithm for when multiple harmonics excitation is used.

4.1 Acknowledgment
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References:
[1] G. Sauerbrey, The use of quartz oscillators for weighing layers and for micro-weighing, *Zeitschrift Fuer Physik,* Vol.155 ,1959, pp. 206-222.

[2] A. Arnau, *Piezoelectric Transducers and Applications*, second edition, Springer-Verlag Berlin Heidelberg, 2008

[3] M. Voinova, On Mass Loading and Dissipation Measured with Acoustic Wave Sensors: A Review, *Journal of Sensors,* 2009

[4] V. Mecea, Is quartz crystal microbalance really a mass sensor? , *Sensors and Actuators,* Vol. 128, 2006, pp. 270–277.

[5] M. Cooper, A survey of the 2001 to 2005 quartz crystal microbalance biosensor literature: applications of acoustic physics to the analysis of biomolecular interactions, *Journal of Molecular Recognition*, Vol.20, 2007, pp. 154–184.

[6] V. Mecea, Loaded vibrating quartz sensors, *Sensors and Actuators*, Vol.40, 1994, pp.1-27

[7] C. Lu and O. Lewis, Investigation of Film-Thickness Determination by Oscillating Quartz Resonators with Large Mass Load, *Journal of Applied Physics*, vol. 43, 1972, pp. 4385.

[8] K. Kanazawa, The oscillation frequency of a quartz resonator in contact with a liquid, *Anal. Chim. Acta*, Vol.175, 1985, pp. 99-105.

[9] M. Voinova, Viscoelastic acoustic response of layered polymer films at fluid-solid interfaces: Continuum mechanics approach, *Physica Scripta*, Vol.59, 1999, pp. 391-396.

[10] D. Johannsmann, Viscoelastic properties of thin films probed with a quartz-crystal resonator, Physical Review B, Vol.46, 1992, pp. 7808-7815.

[11] A. Arnau, A Review of Interface Electronic Systems for AT-cut Quartz Crystal Microbalance Applications in Liquids, Sensors 2008, Vol.8, 2008, pp. 370-411.

[12] M. Rodahl, Quartz crystal microbalance setup for frequency and Q-factor measurements in gaseous and liquid environments, *Review of Scientific Instruments*, Vol. 66, pp. 3924-3930.

[13] K. Kanazawa, Analyzing spur-distorted impedance spectra for the QCM, *Journal of Sensors*, 2009

[14] M. Edwardsson, A dual-frequency QCM-D setup operating at elevated oscillation amplitudes, Analytical Chemistry, Vol.77, 2006, pp. 4918-4926.

[15] T. Pearce, *Handbook of Machine Olfaction*, Wiley-Vch Verlag GmbH & Co, 2003.

[16] K. Jaruwongrungse, Analysis of Quartz Crystal Microbalance Sensor Array with Circular Flow Chamber, *International Journal Of Applied Biomedical Eng.*, Vol.2(2), 2009, pp. 50-54.

[17] S. Pantalei, Enhanced Sensory Properties of a Multichannel Quartz Crystal Microbalance Coated with Polymeric Nanobeads, *Sensors*, Vol.7, 2007, pp. 2920-2928.

[18] A. Tuantranont, A review of monolithic multichannel quartz crystal microbalance: A review, *Analytica Chimica Acta*, Vol.687, 2011, pp. 114–128.

[19] S. Micut, E-NOSE Type Devices, *Lucrarile sesiunii de comunicari stiintifice “Doctor ETc 2009”*, 2009, pp. 61-66.

[20] H. Saraoğlu, E-Nose System for Anesthetic Dose Level Detection using Artificial Neural Network, *Journal of Medical Systems*, Vol.31, 2007, pp. 475-482.

[21] A. Peter, Real-life application of a QCM-based e-nose:quantitative characterization of different plant-degradation processes, *Analytical and Bioanalytical Chemistry*, Vol.391, 2008, pp. 2897–2903.

[22] E. Zampetti, Use of a multiplexed oscillator in a miniaturized electronic nose based on a multichannel quartz crystal microbalance, *Sensors and Actuators B*, Vol.131, 2008, pp. 159–166.

[23] M. Ferrari, Dual-harmonic oscillator for quartz crystal resonator sensors, Sensors and Actuators A: Physical, Vol.145-146, 2008, pp. 131-138.