

A high-performance measurement system for simultaneous mass and resistance variation measurements on gas sensing polymer films

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Abstract

This paper describes a high-performance system set-up for measurements with gas sensitive polymeric layers. The polymeric films are deposited on prototypal Quartz Crystal Microbalance sensors that allow both quartz frequency resonance variation and polymer resistance measurements. This capability adds new dimensions to the feature space allowing the improvement of the system performance. The measurement system is able to simultaneously measure the polymer resistance as well as the QCM frequency variation with high resolution ($<2 \Omega/60 \text{ k}\Omega$ and $<0.1 \text{ Hz}/10 \text{ MHz}$) and fast sampling rate ($\approx 20 \text{ ms}$).

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Keywords: QCM sensors; Conducting polymers; Electronic nose; IEEE 1451.4

1. Introduction

Classification of chemical compounds and gas mixtures is of great interest in many applications like food packing, aroma classification and environmental monitoring. The use of artificial olfactory systems, that are often called “electronic noses”, is one of the common approaches used to accomplish this task. Conductive polymer [1,2,8] and ‘yielded’ conductive (e.g. carbon-black polymers [7]) films are among the gas sensing elements most commonly and widely used in such systems. Polymer films are very attractive for vapor/odor sensing applications because of the wide range of available materials and the ease of deposition, the ability to operate at room temperature (i.e. low device power consumption), and sensitivity to a broad range of volatile organic compounds. Usually polymeric layers are used to realize conductive sensors, for which a change in the sensor

resistance is monitored while the sensor is exposed to the gas.

The polymer mass change upon exposure to gases is also exploited in electronic olfactory systems based on Quartz Crystal Microbalance (QCM) sensors. For this type of sensors, the frequency shift due to the gas sorption, and hence to the mass change, is the measured quantity. This parameter can be measured by means of simple equipment but significant sensor performance improvements can be obtained when exploiting the dynamical behavior of the resonance frequency [3]. This must be accomplished by using sophisticated measurement equipment such as the one presented in [3]. Moreover, a further improvement can be obtained with the simultaneous measurement of the polymer resistance as well as the QCM frequency [17,18]. Nevertheless, this opportunity is rarely exploited. This paper presents a custom sensor class and a measurement system able to simultaneously track the two mentioned quantities with a very high resolution, both for frequency ($<10 \text{ ppb}$) and resistance ($<30 \text{ ppm}$) measurements, and fast sampling rate.

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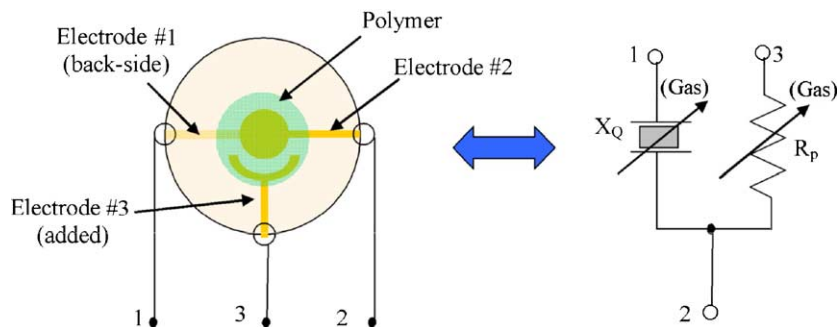


Fig. 1. Prototypal QCM (PQCM) sensor with a third electrode added for the resistance measurement (left) and its equivalent circuit (right).

2. Measurement system

2.1. Sensors

Prototypal QCM sensors (PQCM), that present a third electrode for the resistance measurement of the polymeric sensing film, were prepared for this work by the Institute of Clinical Physiology of Pisa (IT), National Research Council of Pisa. A quartz crystal circular plate ($\varnothing 14$ and 0.18 mm of thickness) containing pre-printed parallel gold electrodes was purchased by Nuova Mistral S.p.A. [5] and added with a third gold electrode for the resistance measurement by vacuum evaporation (Fig. 1). Different types of conducting polymer sensors were prepared by chemically doping poly(3,3'-dipentoxy-2,2'-bithiophene) (dimer in in Table 1) and poly(3,3'-dipentoxy-2,2':5,2''-terthiophene) (trimer in in Table 1) with different inorganic salts at various levels as previously reported [4]. Fabrication was accomplished by depositing with a pipette 1 μ l of doped polymer suspension in chloroform on the quartz crystal and spinning the sensor at 1000 rpm until a uniform coating polymer layer was obtained.

2.2. System set-up

In this paper, a high-performance measurement system, based on the prototypal sensors described above, which is able to simultaneously measure the polymer resistance and the quartz frequency shift with a resolution higher than 30 ppm and 10 ppb, respectively, and sampling rate of 20 ms, is presented. The PC-based system has a modular structure (Fig. 2) and it can manage up to eight modules whose block diagram is sketched in Fig. 3.

Each module manages one PQCM and is composed by two sub-sections dedicated to the frequency and resistance measurement. Within each sub-section an EEPROM (TEDS

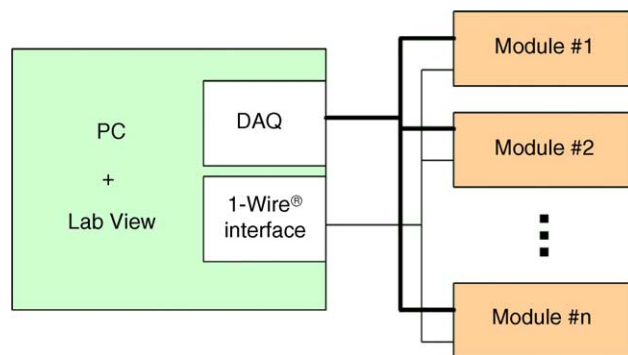


Fig. 2. Set-up of the PC-based olfactory system.

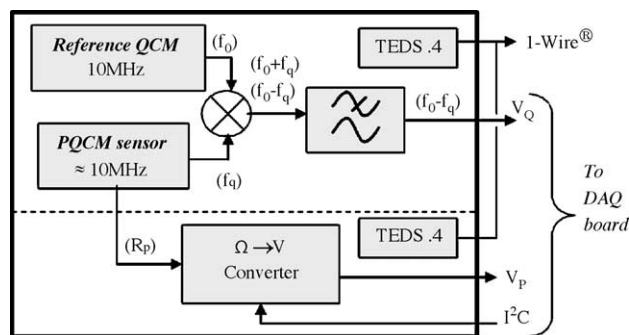


Fig. 3. Module for the accurate frequency and resistance measurement with PQCM sensor. Two EEPROM (TEDS = Transducer Electronic Data Sheet) allow the storage of sensor and front-end parameters in the standard format defined by IEEE 1451.4 standard, giving to the module a “plug and play” characteristic [9].

in Fig. 3), to store sensor and front-end electronics parameters in the format depicted by IEEE 1451.4 standard, is present [9]. The information contained in the TEDSs allows for each module to become “plug and play”. Some details of the stan-

Table 1
Polymer type, doping salt and initial resistance value for the sensors tested

Features	Q_5	Q_{13}	Q_{14}	QA
Polymer	Dimer in	Trimer in	Trimer in	Dimer in
Dopant	$FeCl_3 \cdot 6H_2O$	$FeCl_3 \cdot 6H_2O$	$Cu(ClO_4)_2 \cdot 6H_2O$	$Cu(ClO_4)_2 \cdot 6H_2O$
R_0 (k Ω)	0.38	67.2	0.33	21
f_0 (Hz)	9990187	9984727	9933562	9967720

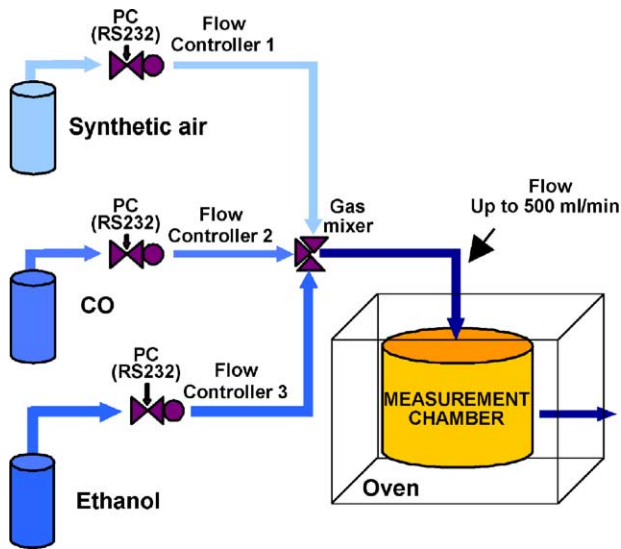


Fig. 4. The automated gas sampling unit.

standard are given below, in this section. The whole system is managed by a Virtual Instrument (VI), implemented with the graphical programming language Labview [10].

The main VI also manages the gas-sampling unit (Fig. 4) that is a digitally controlled system providing the possibility to inject the desired gas or gas mixture into the measurement chamber and to control the gas flow (up to 500 ml/min) by means of three mass-flow controllers. The sensors (up to 4) are arranged in a cylindrical symmetry configuration orthogonal to the gas flow, so that each of them receives in parallel the same amount of gas. The measurement chamber is made of polytetrafluoroethylene (PTFE) and kept inside an incubator for precise temperature measurement and control.

The high frequency measurement resolution is obtained by the particular technique adopted. The PQCM frequency $f_q(\text{gas})$ is shifted by means of a mixer device and a reference (not coated) QCM, with a resonance frequency f_0 , as illustrated in Fig. 3. The mixer device provides at the output two signals with frequency $(f_q(\text{gas}) + f_0)$ and $(f_0 - f_q(\text{gas}))$ given by the inter-modulation product. The low-pass filter allows for eliminating the higher frequency signal. The shift frequency value, $(f_0 - f_q(\text{gas}))$, is usually lower than 30 kHz. Usually, a sample frequency of 60 kS/s is adequate. The 'low frequency' signal V_Q is acquired by the PC through a data acquisition board (PCI-MIO-16-E-1 by National Instrument [10]). A sub-VI performs the frequency estimation with resolution lower than 0.1 Hz when the input signal presents a $S/N = 60$ dB. The algorithm is based on the FFT algorithm and on the assumption of single tone signal. A further advantage of the presented system is the possibility to compensate the frequency variations caused by external factors like e.g. the temperature variation. In fact, both QCMs (sensor and reference) can be placed inside the measurement chamber so they undergo the same temperature.

The polymer resistance measurement is accomplished by using a quarter bridge configuration (Fig. 5). The bridge is

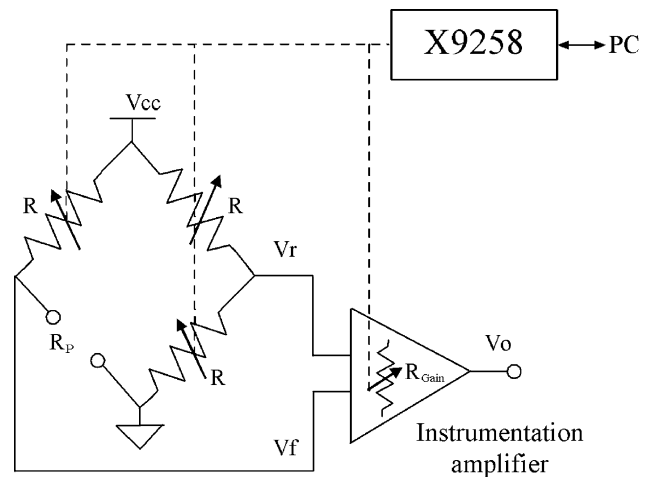


Fig. 5. Scheme of the section for accurate polymer resistance measurements which makes use of digital potentiometers for bridge balancing and signal amplification setting.

automatically balanced by means of three digital potentiometers that can be set through the I²C bus controlled by the main VI. The digital potentiometers are implemented by X9258 IC [6] that contains four digitally programmable resistors with maximum resistance of 100 k Ω and resolution 0.4%. The X9258 is univocally recognized along the I²C parallel bus by a user-defined chip address (4 bits) that allows connecting in parallel up to 16 devices. The differential output $V_r - V_f$ is amplified by an instrumentation amplifier whose gain can be trimmed by the fourth digital potentiometer contained in the X9258 (maximum gain = 256). The output signal V_P is acquired by the DAQ and processed by the PC. This configuration allows reaching a resistance measurement resolution of 30 ppm which is necessary to detect and track the weak resistance variation caused by low gas concentration or low polymer sensitivity.

2.3. Standard for Smart Transducer, IEEE 1451 and IEEE 1451.4

The IEEE 1451 standard is divided into several sub-projects named IEEE 1451.0 (dot 0), IEEE 1451.1 (dot 1) and so on up to IEEE 1451.6 (dot 6). Some of them are approved standards (dot 1, approved in 1999 [11], dot 3 and dot 4 both approved in 2004) while the other are Proposals. The IEEE 1451.2 was first approved in 1997 [12] but it is under revision since 2004. This part of the Standard has defined a 10-wires bus and the relative protocol. The main innovation introduced by the IEEE 1451.2 was the definition of a Transducer Electronic Data Sheet (TEDS), which is a data structure stored in a small amount of non-volatile memory, physically associated with the transducer. The recent standard IEEE 1451.4 is at the moment quite popular and many companies have already started implementing dot 4-compliant sensors or interface electronics (e.g. National Instruments [10], Dallas-Maxim [13], Bruel & Kjaer, PCB Piezotronics, Watlow, to list a few).

This part of the Standard defines an interface for analogue transducers for mixed-mode operation and defines TEDSs to be associated to the analog transducers that are different from dot 2-TEDS. The dot 4-TEDSs have different structures (templates) according to the type of transducer to which they are associated. For instance, it is defined the generic template for “resistive-output sensor” (Template 32), the generic template for sensors with “high level voltage output” (Template 30), the template specific for “bridge sensors” (Template 33), and so on. Comprehensive information about dot 4 templates can be found in [10]. The TEDS allows for analogue transducers to communicate digital information for self-identification, self-configuration, self-calibration, and easy manipulation. The analogue transducer, with associated electronics, sends out digital information data upon command through 1-Wire® bus [13] and it senses or controls a physical phenomenon in analogue mode.

Since there are no templates for gas sensors, one should consider the polymer as a resistive sensor or, in our case, as a bridge sensor. The QCM sub-section can be seen as a “Voltage output” sensor. The module depicted in Fig. 3 can be considered as the first prototype of Standard gas sensor compliant with the IEEE 1451.4. The TEDSs are written through 1-Wire® interface (Fig. 3) by using dedicated VIs. A study to define templates for gas sensors is on the way as well as the design of a full self-configurable olfactory electronic system based on “plug and play” gas sensors.

3. Experimental results

The measurement system was tested by using a PQCM (Q_{13}) and an uncoated QCM (‘blank’ QCM, Q_{BL}). Effects of environmental conditions such as temperature and gas flow variations were investigated by analyzing the Q_{BL} behavior. For this purpose the reference quartz (needed to carry out the differential measurement) for Q_{BL} was placed outside the measurement chamber but inside the oven in order to maintain a constant temperature and to avoid flow effects. In fact, we remind here that the frequency of the output signal V_Q (Fig. 3) is the difference between the resonant frequencies of Q_{BL} and the reference quartz. The reference quartz for Q_{13} was placed inside the measurement chamber to account for the above-mentioned environmental variations.

Table 2
Test gases and gas mixtures (hereafter each sample will be addressed with the number reported in the corresponding table cell)

Ethanol (ppm, v/v)	CO (ppm, v/v)			
	0	100	200	500
0		#1	#2	#3
200	#4			#7
400	#5			
800	#6			

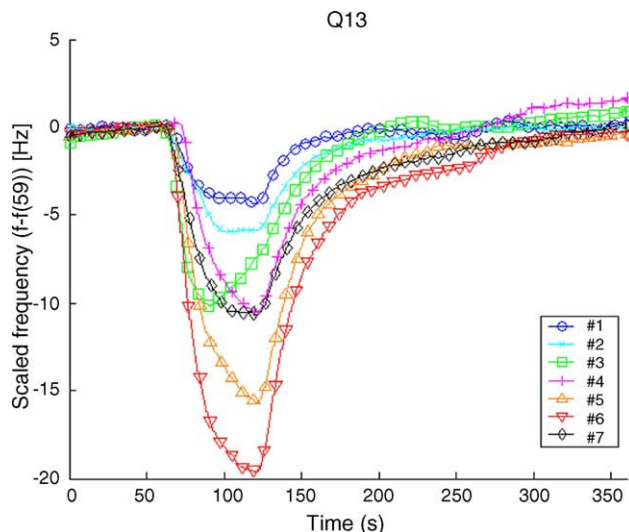


Fig. 6. Frequency shift, normalized to 10 MHz, of the Q_{13} sensor when exposed to test samples listed in Table 2. Only one response per class is shown for graphical reasons.

The gas mixtures used for this work are listed in Table 2 with their relative concentrations. The measurement protocol was: exposure to reference gas (synthetic air, duration 60 s), exposure to the gas under test (60 s) and recovery in synthetic air (240 s). A constant airflow value of 200 ml/min was used.

The Q_{13} frequency responses to the various samples are shown in Fig. 6. The frequency value measured in the reference synthetic air just before the gas is injected into the chamber (59 s) was considered as the baseline value and subtracted to the subsequent data points (scaling). Only one response per class is shown for graphical reasons. The Q_{13} scaled resistance responses are shown in Fig. 7. The baseline

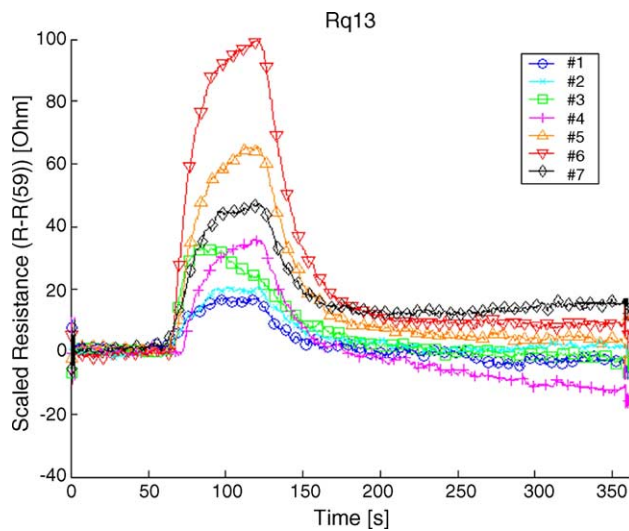


Fig. 7. Resistance shift, normalized to the value for the reference gas of the Q_{13} sensor when exposed to test gases and mixtures listed in Table 2. Only one response per class is shown for graphical reasons.

resistance of the polymer films deposited on Q_{13} is about $67\text{ k}\Omega$ (see Table 1).

It can be observed that the maximum frequency shift is given by the maximum concentration of ethanol (#6) and it is below 20 Hz ($\approx 2\text{ ppm}$). The need of a high resolution even for the resistance measurement is evident from Fig. 7 where a maximum resistance change of about $100\ \Omega$ ($\approx 1670\text{ ppm}$) is also observed for gas #6.

It is interesting to notice that sensor responses (both resistance and frequency) to gas concentration greater than 200 ppm of carbon monoxide (CO) show a peculiar change of slope around 20 s after the gas injection.

Data analysis of Q_{13} responses and gas recognition cannot be accomplished by using traditional feature extraction techniques such as the maximum shift since responses to different gases (e.g. #3, #4, #7 in Fig. 6, #3, #4 and #1, #2 in Fig. 7) give similar values. Also the single-exponential fitting technique [14,15] is not suitable for this application since the not-single-exponential-like responses to CO. For the present study, two integrals of the responses calculated between the gas injection (60 s) and 85 s (ell in responses to CO) and 120 s (start of recovery), were used. These parameters are robust to measurement noise and take into account the response shape [15]. It can be demonstrated that this technique is also equivalent to the exponential fitting when the responses are single-exponential-like [15].

The principal component analysis (PCA) performed only on the features extracted from frequency responses is shown in Fig. 8. In the PCA plot is also reported the “Loadings plot” (LP# in figure) related to the features. The Loadings show the influence of each feature onto the principal components. They give information about the “importance” of a feature (features not contributing will be near the centre while LPs far from origin will be more significant) and correlation among

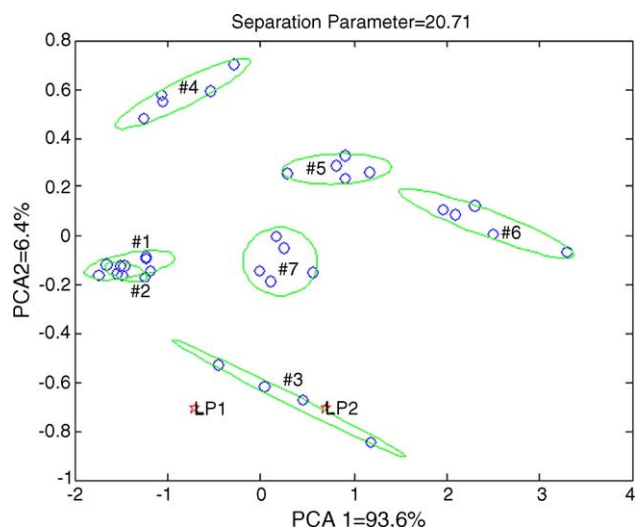


Fig. 8. PCA performed on the Q_{13} frequency response to the gas mixtures listed in Table 2.

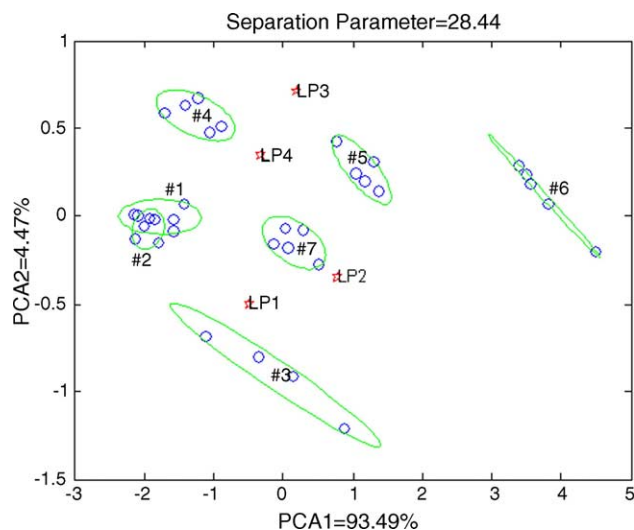


Fig. 9. PCA performed on the Q_{13} polymer resistance and frequency responses to the gas mixtures listed in Table 2.

features (LP with similar information will be represented next to each other) [16].

Fig. 8 suggests that gas and gas mixtures recognition might be possible even by using only frequency information. Only class #1 cannot be distinguished from class #2 indicating a resolution worse than 100 ppm of CO at low concentrations. Ellipses are drawn in Fig. 8 around gas classes with axes lengths equal to two times the class standard deviation in the radius direction. The ellipses are found by performing PCA of data belonging to a single class, and highlight the direction of maximum variability of each class. To obtain a measure of the quality of the measurement, a separation parameter SP was defined as the sum of the ratios between minimum class centroid distance and ellipses areas. The separation parameter is normalized with respect to the number of classes. For the PCA of Fig. 8 we obtain $SP = 20.71$. This parameter allows also comparing analysis performed with different number of parameters and different feature extraction techniques.

Fig. 9 shows the PCA performed on the same gases but where also the resistance information is used. In this case, the separation parameter is higher than the previously illustrated case ($SP = 28.44$ versus $SP = 20.71$ with only frequency).

The responses of the blank QCM Q_{BL} to the different mixtures are shown in Fig. 10. Also in this case only one response per class is shown for graphic clarity. It is interesting to observe that a slight frequency (always $< 1\text{ Hz}$) change occurs even without sensing film. This could be due to the valve switching and to the not-ideal response of the mass-flow controllers managing the chemical transient, causing a temporary change of pressure into the chamber, and even to the gas adsorption on the gold metal plates. It must be noted that this effect can be revealed only thanks to the high system resolution and, moreover, such responses are not negligible when the PQCM response is weak. To understand the actual reasons of the frequency variation of Q_{BL} , a chemical tran-

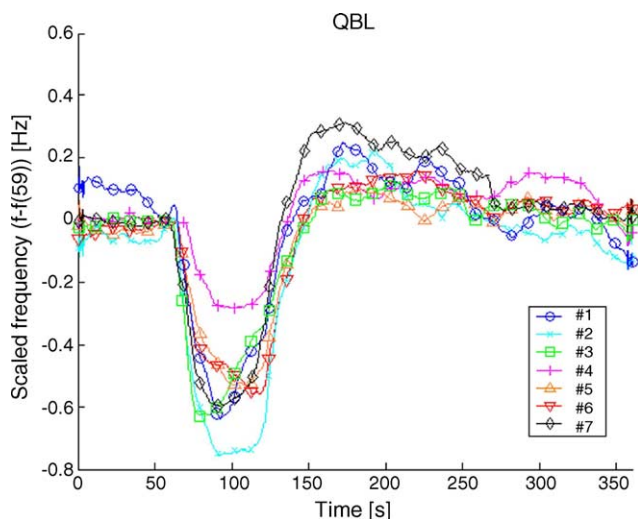


Fig. 10. Frequency response of Q_{BL} (not coated with sensing film) to the gas mixtures listed in Table 2.

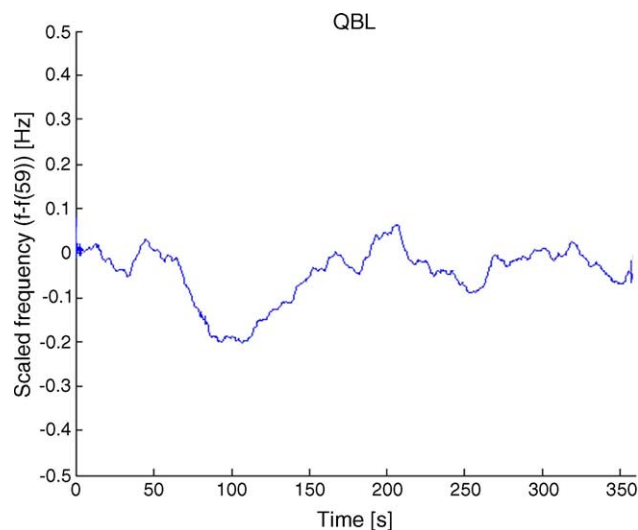


Fig. 11. Frequency response of Q_{BL} (not coated with sensing film) to only synthetic air switched between two lines and by using the same protocol described above.

sient performed by switching between two gas lines with the same reference gas was accomplished. The result of the test is shown in Fig. 11 from which it comes out that the main variations in Fig. 10 are probably due to gas adsorption on the gold metal plates.

4. Conclusion

A high-performance measurement system based on prototypal QCMs that allow simultaneous measurements of the polymer resistance and the quartz frequency shift with a resolution higher than 30 ppm and 10 ppb, respectively, was presented. The system allows to characterize gas sensing

properties of polymeric films and to enhance their sensing performances thanks to the high measurement resolution. The effects of the temperature variations and other external factors can be automatically cancelled by the use of a reference QCM. The test carried out by using only one PQCM suggests high potentiality for gas discrimination even at low concentrations. Future works will be dedicated to the study of various polymer films and will be focused on the research of stability and repeatability of the polymer responses.

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Biographies



Ada Fort received the Laurea degree in Electronic Engineering from the University of Florence, Italy, in 1989. She received the PhD degree in non-destructive testing from the same university in 1993. Since 1997 she joined the University of Siena, where she is currently associate professor of Electrical and Electronic Measurements. Her current interests concern the development of measurement systems based on chemical sensors, and the development of automatic fault diagnosis systems.



Santina Rocchi received the Laurea degree in Electronic Engineering from the University of Florence in 1978. From 1981 to 1992 she was an Assistant Professor of Electronics at the University of Florence, where she was involved in the development of prototype systems for ultrasonic applications in medical diagnosis, non-destructive testing and robotics. In 1992, for 1 year, she was an Associate Professor of Electronics at the University of Perugia. Since 1993 she joined the University of Siena, where she is currently full professor of electronics at the Department of Information Engineering. Her main research interest is sensor front-end and processing electronics design, with emphasis on chemical, optical and acoustic sensors.



M. Belén Serrano Santos received Graduate degree in Physical Chemistry at the Complutense University of Madrid and Maîtrise in Solid State Chemistry at the University of Paris-Sud in 1993. She received PhD degree at the University of Siena in 2000 for her work on synthesis and structural characterization of natural and synthetic silicates with molecular sieving properties. She currently works at the University of Siena on a laboratory electronic nose as well as on the fabrication of membrane coatings to enhance the selectivity of ceramic sensors.



Nicola Olivieri received his Laurea degree in Telecommunication Engineering at the University of Siena in 1999. In 2003 he received the PhD degree from the University of Siena, Department of Information Engineering, thesis title: “Developing, modelling and integration of olfactory electronic systems”. Since 2003 is a research associate of the Department of Information Engineering of the University of Siena. His main research activity is related to the development of laboratory electronic noses based on metal oxide sensors and QCM sensors. Recently his interests were also devoted to integrated analogue and mixed signal electronics design and smart sensors development.



Valerio Vignoli received the Laurea degree in Electronic Engineering from the University of Florence, Italy, in 1989. He received the PhD degree in non-destructive testing from the same University in 1994. Since 1997 he joined the Department of Information Engineering of the University of Siena (Italy), where he is currently associate professor of Electronics. His current research interests include sensor and smart sensor systems, with particular emphasis in front-end electronics design.



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Fabio Di Francesco graduated as a physicist in 1994 from University of Pisa. He worked for 2 years to the development of mercury pollution detection methods at the Institute of Biophysics (National Research Council, CNR), then he joined Interdepartmental Research Center “E. Piaggio” where he started working on electronic noses with two distinct application areas, evaluation of olfactory annoyance of industrial emissions and detection of olive oils defects. At present, he is research scientist at the Institute of Clinical Physiology (CNR) where, within the MAST group, he is responsible for the development and use of electronic noses.