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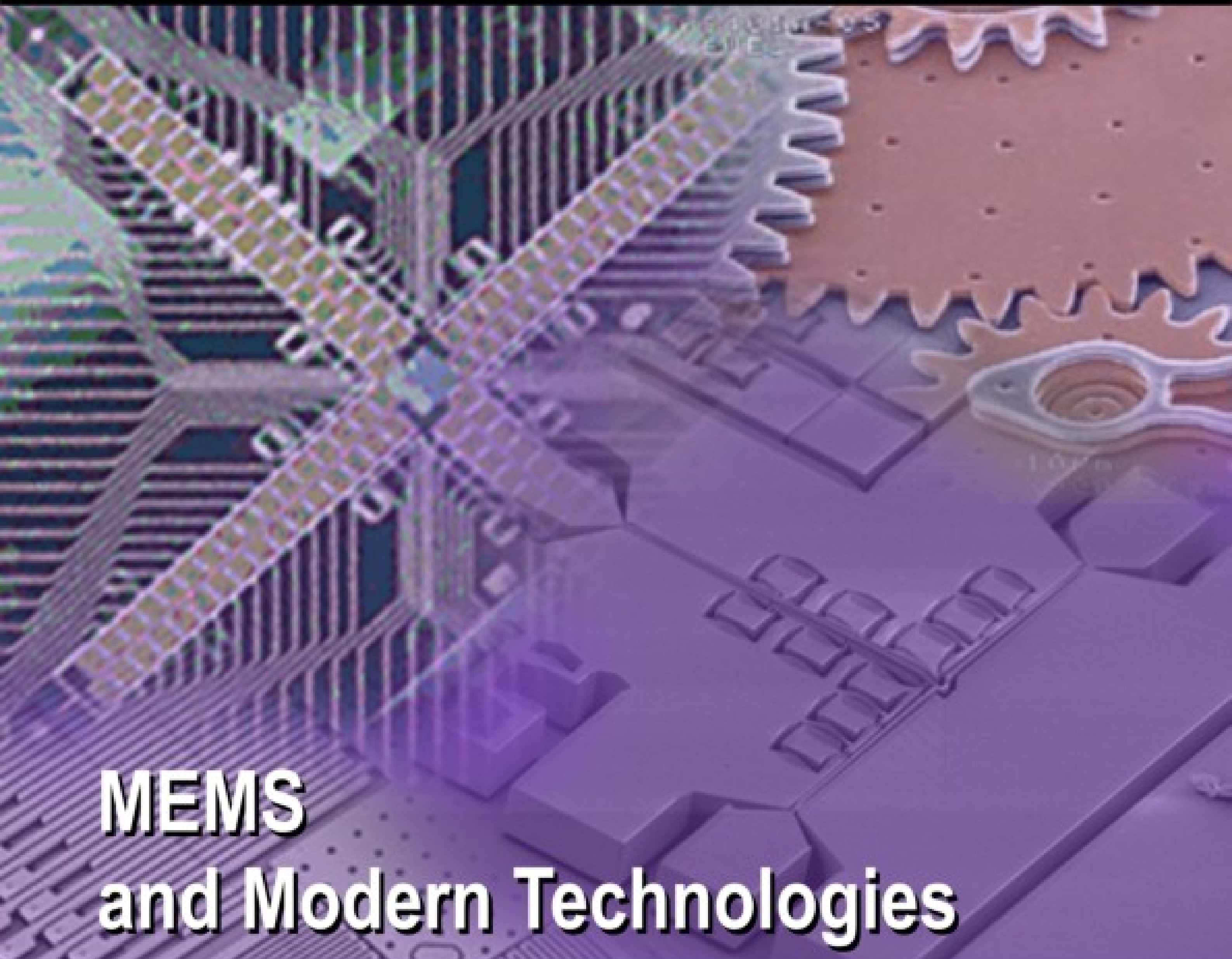

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Odor Sensing With Indium Tin Oxide Thin Films on Quartz Crystal Microbalance

Nirmal PATEL, Jay HUEBNER, Jason SAREDY and Brian STADELMAIER
Department of Chemistry & Physics
University of North Florida, 1 UNF Drive
Jacksonville, Florida 32224, USA
Tel.: 904-620-1670
E-mail: npatel@unf.edu

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Abstract: Odor sensors were fabricated by depositing nanocrystalline Indium Tin Oxide thin films on AT-cut quartz crystals. These sensors were tested with odors from different groups of foods, including fruits, cheeses, and wines. The change in frequency characteristics and surface resistance as a function of time was measured for each. Principal Component Analysis showed intuitive groupings of the odors tested. *Copyright © 2008 IFSA.*

Keywords: Indium-tin oxide thin films, Electronic nose, Odor sensors, Quartz crystal microbalance, Principal component analysis

1. Introduction

Human sensory panels cannot be used to assess many odors, including those of hazardous, toxic, and explosive chemicals. They cannot work continuously for longer time periods or operate remotely. Human smell also has poor sensing reproducibility because of possible infection, fatigue, time of day and prior odors analyzed. Electronic noses consist of arrays of odor sensors [1, 2], which can be applied to measuring and identifying toxic gases, air quality, fuel mixtures, foods [3], cosmetic products, household odors, and narcotic materials. The main motivations for electronic noses are low cost, qualitative, real time, and portable techniques to perform reproducible and reliable measurements of odors and volatile compounds [2]. Table 1 shows the major disadvantages of different types of transducers with appropriate sensitive layers that are currently used to fabricate electronic noses.

Table 1. Major disadvantages of different types of odor sensors.

Type of Odor Sensors	Disadvantages
Spectrometry	There are two types of spectrometry: gas chromatography and mass spectrometry. Spectrometry techniques are expensive, not portable, need longer analysis time and require a skilled operator.
Conductivity	Polymer based conductivity sensors respond relatively slowly to odors [4, 5], have drift problem, are sensitive to humidity [6] and have a short lifetime [7].
Optical fibers	Optical fiber sensors have the disadvantage of slow response time, mainly because the odor molecules interact slowly with the chemically active fluorescent dye to change its polarity, short lifetime due to photo bleaching [8] and higher cost because of complex electronics and software.
MOSFET	MOSFET sensors require the odor reaction product to penetrate the gate to produce any response. Therefore, a porous gas sensitive gate material is required [9].
Piezoelectric Crystal: SAW	There are two categories of Piezoelectric sensors: Surface acoustic wave (SAW) device and quartz crystal microbalance. SAW sensors use a Rayleigh wave that travels along the surface of the sensor, while the QCM produces a wave that travels through the bulk of the sensor. SAW sensors have the disadvantage of poor signal to noise ratio because of larger surface to volume ratio [7] and complex and expensive circuits required to operate it [10].

Quartz crystal microbalance (QCM) sensors can be selective and sensitive [10], stable over wide temperature ranges, have low response to humidity, good reproducibility, faster response time [11], and linear characteristics over a wide dynamic range. The detection of explosive materials in passenger luggage, toxins, bacteria, decay in food materials and lung diseases requires highly sensitive and selective odor sensors. Metal oxide sensors have been widely studied for gas sensing applications but have the main disadvantage of requiring a high operating temperature [10]. Patel et al reported application of Indium Tin Oxide (ITO) thin film sensors for the detection of several gases, including volatile organic compounds, at room temperature, which do not require heaters [12-14]. In the present study, the ITO thin films are applied over commercial quartz crystals for use in Stanford Research Systems (SRS) QCM200. The preliminary results of these ITO-QCM sensors are highlighted in this paper.

2. Working Principles

A QCM sensor comprises a quartz crystal coated with a chemically sensitive ITO thin film as shown in the Fig.1. The crystal has a fundamental frequency of 5 MHz. When vapors or odors from the sample interact with the coated ITO thin film, some are adsorbed, causing an increase in the mass of the film which in turn decreases the resonance frequency.

The sensitivity of QCM is given by the following Sauerbrey's equation [15], where *m* is the mass, *f* is the fundamental frequency and *A* is the area of the sensitive film.

$$\frac{\Delta f}{\Delta m} = \frac{(-2.3x10^{-6})}{A} f^2 \quad (1)$$

The SRS QCM200 used also measures the change in the surface resistance of the quartz crystals, which is proportional to viscosity changes at the interfaces.

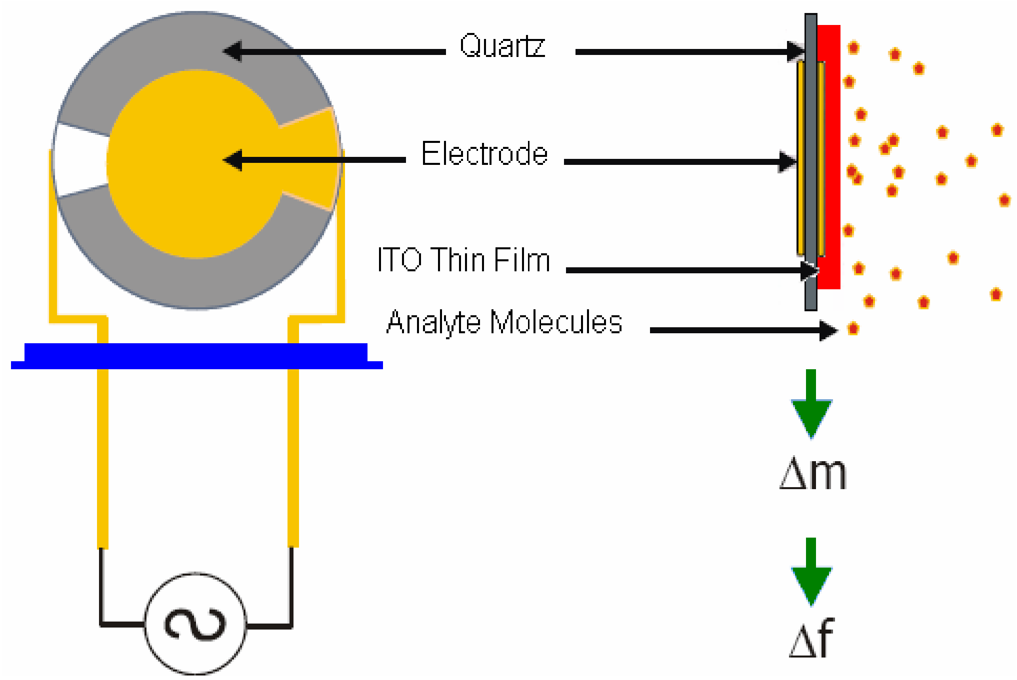

Fig. 1. Schematic diagram of ITO-QCM sensors.

3. Experimental

A Stanford Research Systems (SRS) QCM200 with 5MHz crystals was used in the present study. Thin films of ITO were deposited over the gold-sputtered quartz crystals at a 250°C substrate temperature. The thicknesses of the ITO films were varied from 100 to 300 nm. A Scanning Electron Microscope (SEM, FEI Quanta 200) was used to show the ITO films have a nanocrystalline structure, as shown in Fig.2. The chemical composition was verified using the EDAX (Energy Dispersive X-Ray Spectroscopy) unit attached to the SEM. The ITO coated crystals were mounted in the crystal oscillator holder, which was connected with a digital controller and a computer. The data was collected using LabVIEW (National Instruments). The crystal holder containing the ITO-QCM sensor was kept in a 500ml glass jar for the testing of odors. An equal mass of crushed fruit samples was applied over one end of thick paper strips. Each paper strip was inserted in the test jar and kept 2 cm above the surface of the ITO film for 10 seconds, and then removed from the jar. A new paper strip was used for each run of each test sample.

4. Measurements

The changes in frequency and surface resistance as a function of time were recorded as odor molecules were adsorbed on the ITO film, and then desorbed after the samples were removed from the jar. Measurements were taken for 9 assorted fruits, 6 apples, 4 orange and tangerine samples, 3 cheeses (Kraft), 6 onion and garlic samples, and 3 wines. The variable parameters are illustrated in Fig. 3.

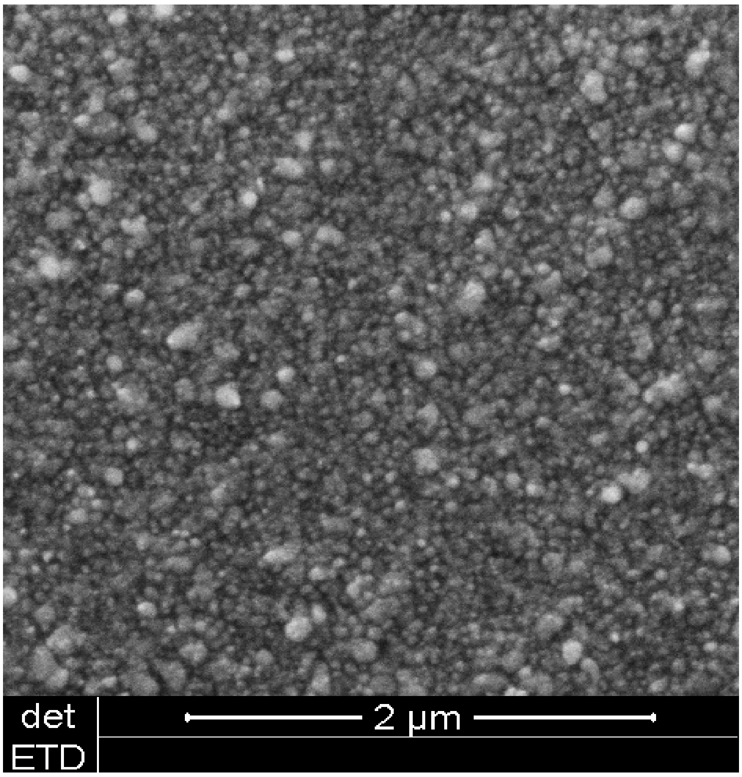

Fig. 2. Scanning electron micrograph of the ITO thin film.

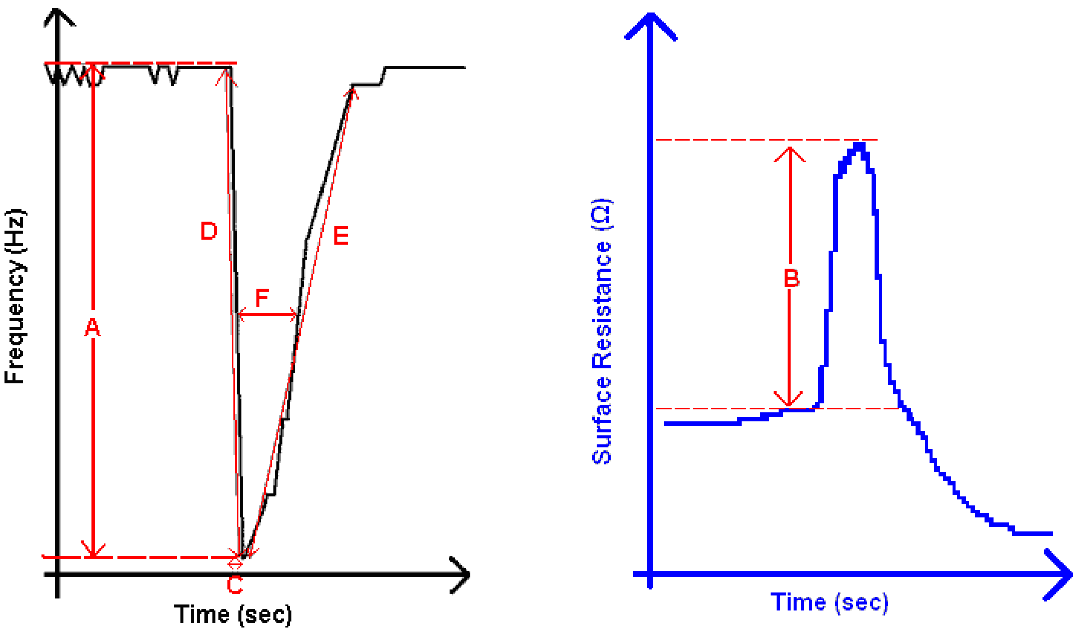

Fig. 3. Illustration of measured parameters on the frequency and surface resistance vs. time plots, where A-Change in frequency response (Hz), B-Change in surface resistance (Ω), C-Initial response time (sec.), D-Initial response slope (Hz/sec.), E-Return to baseline slope (Hz/sec.), and F-Full width at half maximum (sec.).

The following graphs show the ITO-QCM output when exposed to apples (Fig.4), cheeses (Fig.5), assorted fruits (Fig. 6), onions and garlic (Fig. 7), an orange and tangerine (Fig. 8), and wines (Fig. 9). As shown the ITO-QCM sensor responded with changes in frequency, as well as changes in surface resistance for all odors tested.

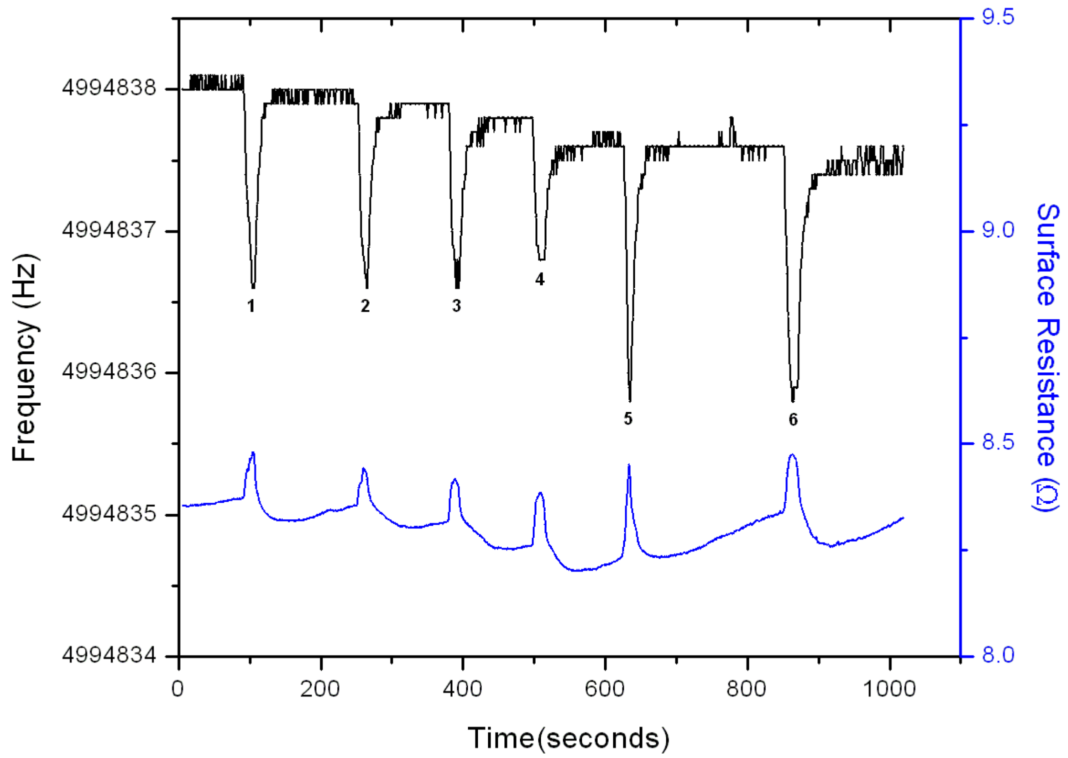

Fig. 4. Change in frequency and surface resistance responses as the ITO-QCM film was exposed to odors from apples: 1-Ambrosia, 2-Red Delicious, 3-Granny Smith, 4-Rome, 5-Jazzenza, and 6-Gala.

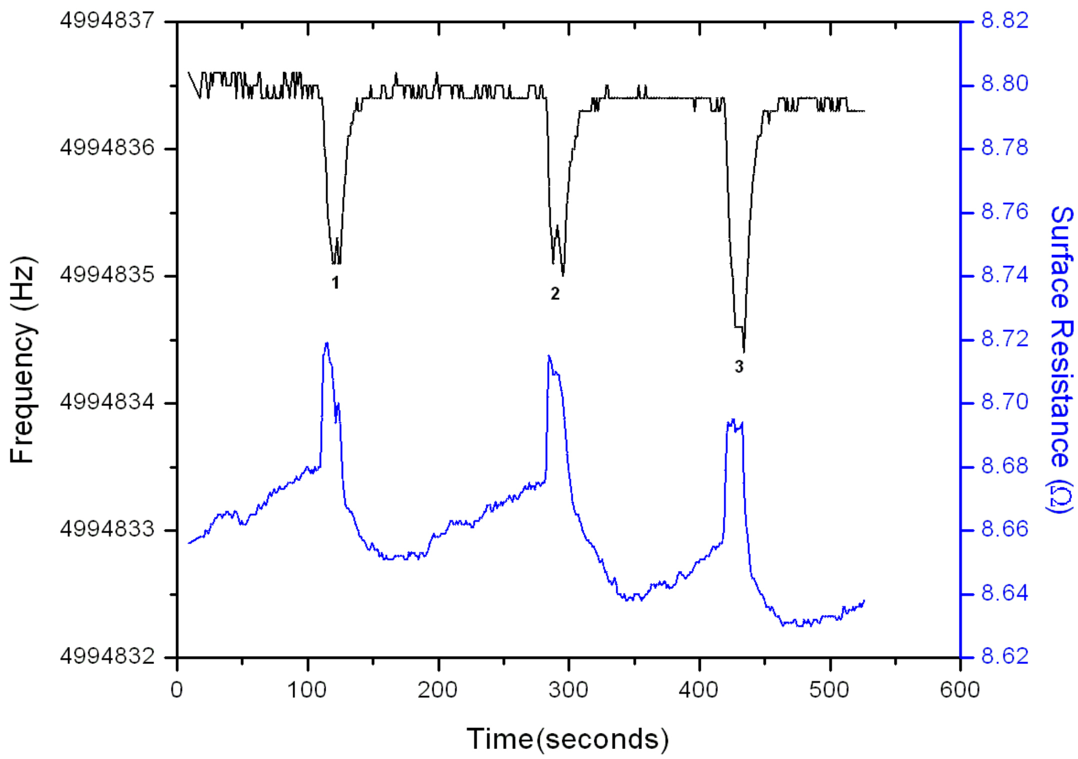

Fig. 5. Change in frequency and surface resistance responses as the ITO-QCM film was exposed to odors from cheeses: 1-Cheddar, 2-Swiss, and 3-American.

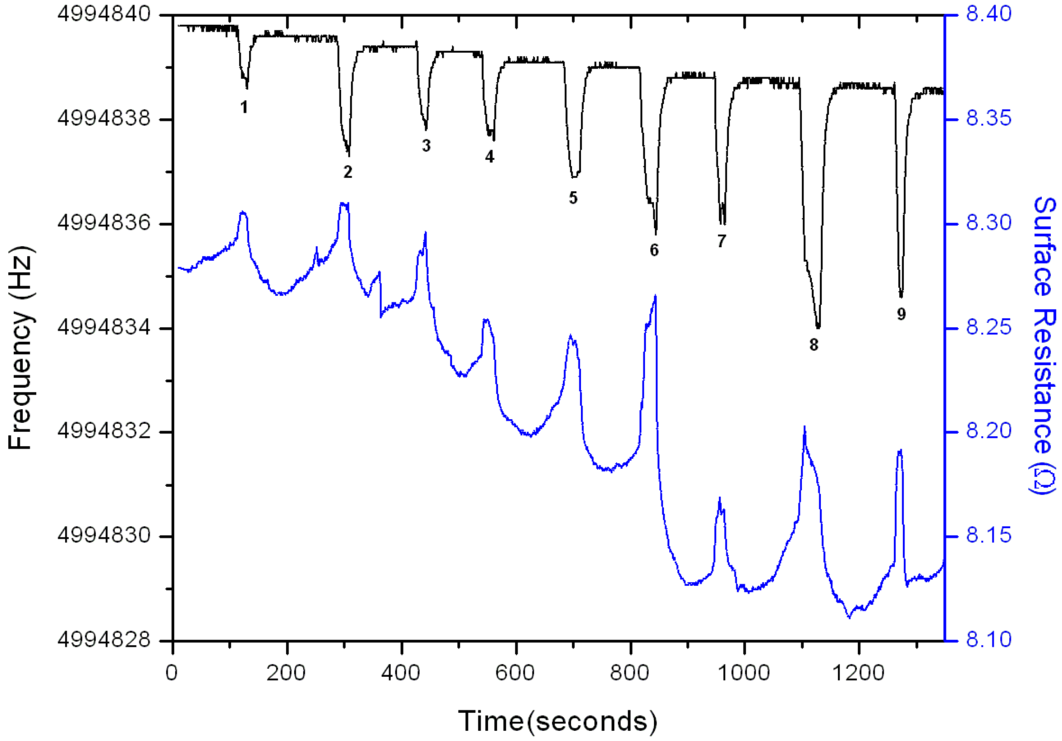

Fig. 6. Change in frequency and surface resistance responses as the ITO-QCM film was exposed to odors from assorted fruits: 1-Kiwi, 2-Mango, 3-Papaya, 4-Pineapple, 5-Strawberry, 6-Honeydew, 7-Cantaloupe, 8-Watermelon, 9-Red grape.

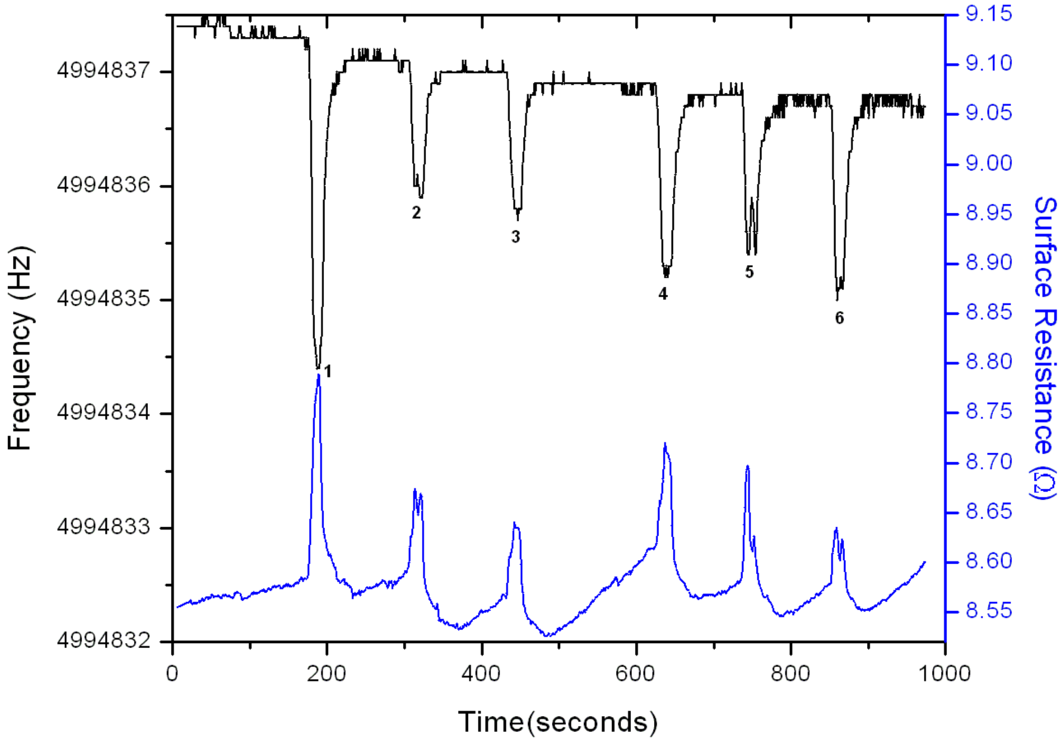

Fig. 7. Change in frequency and surface resistance responses as the ITO-QCM film was exposed to odors from onions and garlic: 1-Red onion, 2-Yellow onion, 3-White onion, 4-Garlic outer shell, 5- Garlic inner shell, and 6-Garlic core.

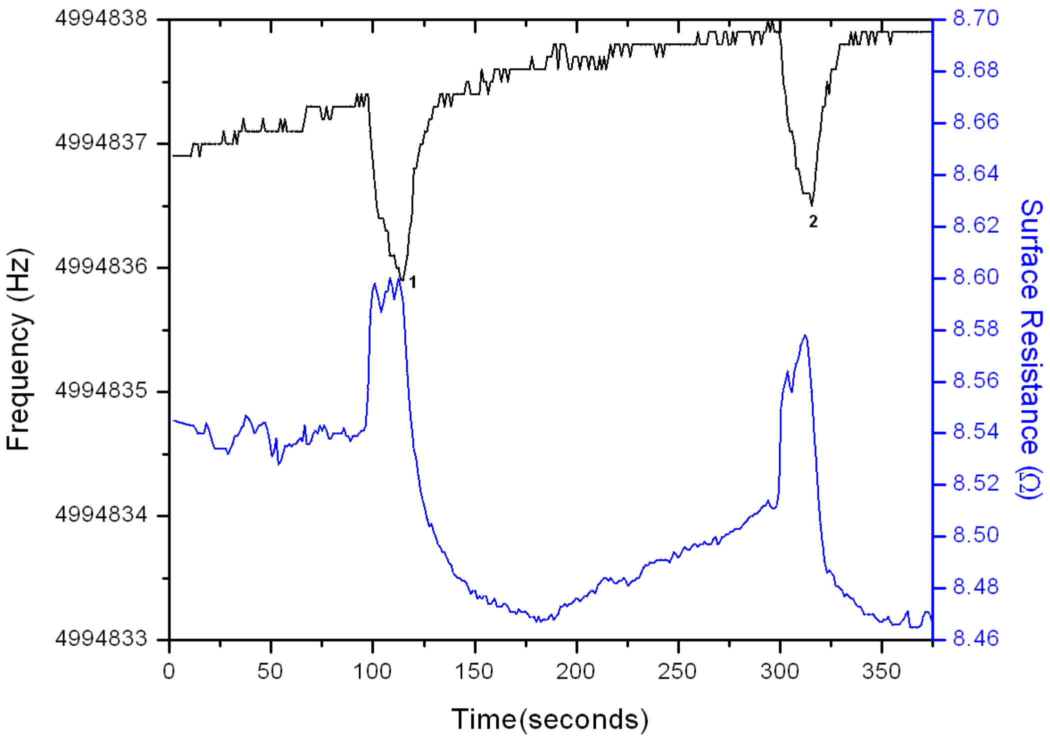

Fig. 8. Change in frequency and surface resistance responses as the ITO-QCM film was exposed to odors from an orange and tangerine: 1-Navel orange, and 2-Tangerine.

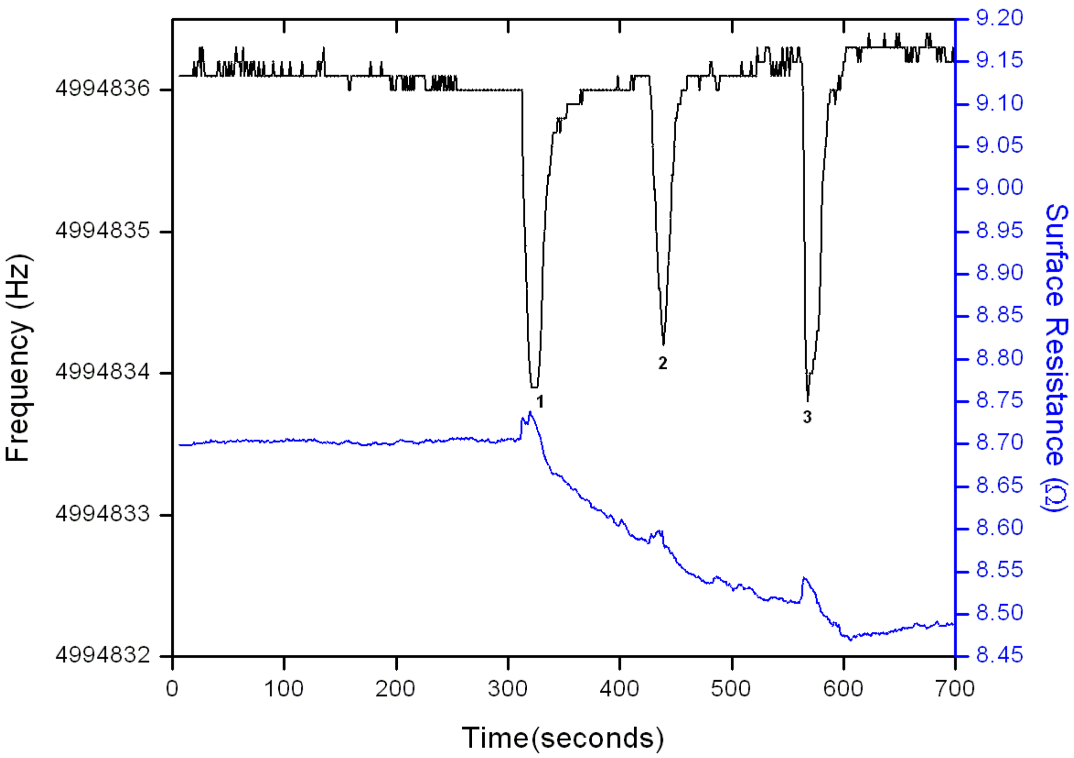

Fig. 9. Change in frequency and surface resistance responses as the ITO-QCM film was exposed to odors from wines: 1-White Merlot, 2-White Zinfandel, and 3-Pinot Grigio.

A summary of all ITO-QCM measured parameters that were obtained from the raw data files plotted in Figs. 4 to 9 is shown in Table 2.

Table 2. Raw data parameters chart for all food odors measured with ITO-QCM.

Analyte	Change in frequency response (Hz)	Change in resistance response (Ω)	Initial response time (sec)	Initial response slope (Hz/sec)	Return to baseline slope (Hz/sec)	Full width half maximum (sec)
Kiwi	1.2	0.016	16.1	-0.075	0.149	17.7
Mango	2.3	0.018	22.5	-0.102	0.186	20.1
Papaya	1.7	0.031	17.2	-0.099	0.110	17.9
Pineapple	1.6	0.018	20.4	-0.078	0.135	22.7
Strawberry	2.2	0.029	15.0	-0.146	0.147	26.3
Honeydew	3.2	0.074	29.0	-0.110	0.186	25.6
Cantaloupe	2.9	0.036	17.2	-0.169	0.203	19.2
Watermelon	4.8	0.044	31.1	-0.154	0.241	34.2
Red grape	4.1	0.055	10.7	-0.382	0.272	13.0
Ambrosia Apple	1.4	0.108	11.8	-0.119	0.112	15.6
Red Delicious Apple	1.3	0.087	11.8	-0.110	0.104	14.2
Granny Smith Apple	1.3	0.101	9.7	-0.135	0.093	16.4
Rome Apple	1.0	0.125	9.7	-0.103	0.080	16.7
Jazzenza Apple	1.8	0.222	8.6	-0.209	0.127	10.0
Gala Apple	1.8	0.139	11.8	-0.152	0.124	18.8
Navel Orange1	1.5	0.060	16.1	-0.093	0.093	18.6
Tangerine1	1.5	0.067	19.3	-0.078	0.114	17.2
Tangerine2	1.5	0.042	13.9	-0.108	0.101	17.6
Navel Orange2	1.2	0.052	10.7	-0.112	0.076	14.7
Red Onion	2.9	0.205	10.7	-0.270	0.179	15.8
Yellow Onion	1.2	0.095	14.0	-0.086	0.120	18.7
White Onion	1.3	0.081	14.0	-0.093	0.085	17.5
Garlic outer shell	1.7	0.104	11.8	-0.144	0.082	19.2
Garlic inner shell	1.5	0.116	7.5	-0.199	0.133	20.5
Garlic core	1.7	0.063	18.2	-0.093	0.161	15.0
Sharp Cheddar Cheese	1.4	0.040	11.8	-0.118	0.101	14.8
Swiss Cheese	1.5	0.040	16.1	-0.093	0.101	15.3
American Cheese	2.0	0.043	25.8	-0.078	0.158	15.5
White Merlot Wine	2.1	0.025	8.6	-0.244	0.129	16.8
White Zinfandel Wine	1.9	0.015	12.9	-0.147	0.132	12.6
Pinot Grigio Wine	2.5	0.030	7.5	-0.333	0.108	15.2
Average (mean)	1.9	0.070	14.9	-0.143	0.134	17.9
Standard deviation	0.9	0.051	6.0	0.075	0.047	4.6

5. Principal Component Analysis

Principal component analysis (PCA) is a statistical analysis procedure which takes multi-variable input data represented by a chart and re-maps the original data onto a new coordinate system that is more efficient at representing the variation contained within the data set. The steps for performing PCA analysis on a chart of data such as that given in Table-2 can be found in statistics and chemo-metrics textbooks [16] and from online sources [17]. Looking at Figs. 4 to 9, the ITO-QCM output measurement graphs, and/or the raw data in Table-2, it seems clear there is no intuitive way to classify the various odors. However PCA allows similarities and differences among the analytes measured to be seen as is shown in Fig. 10.

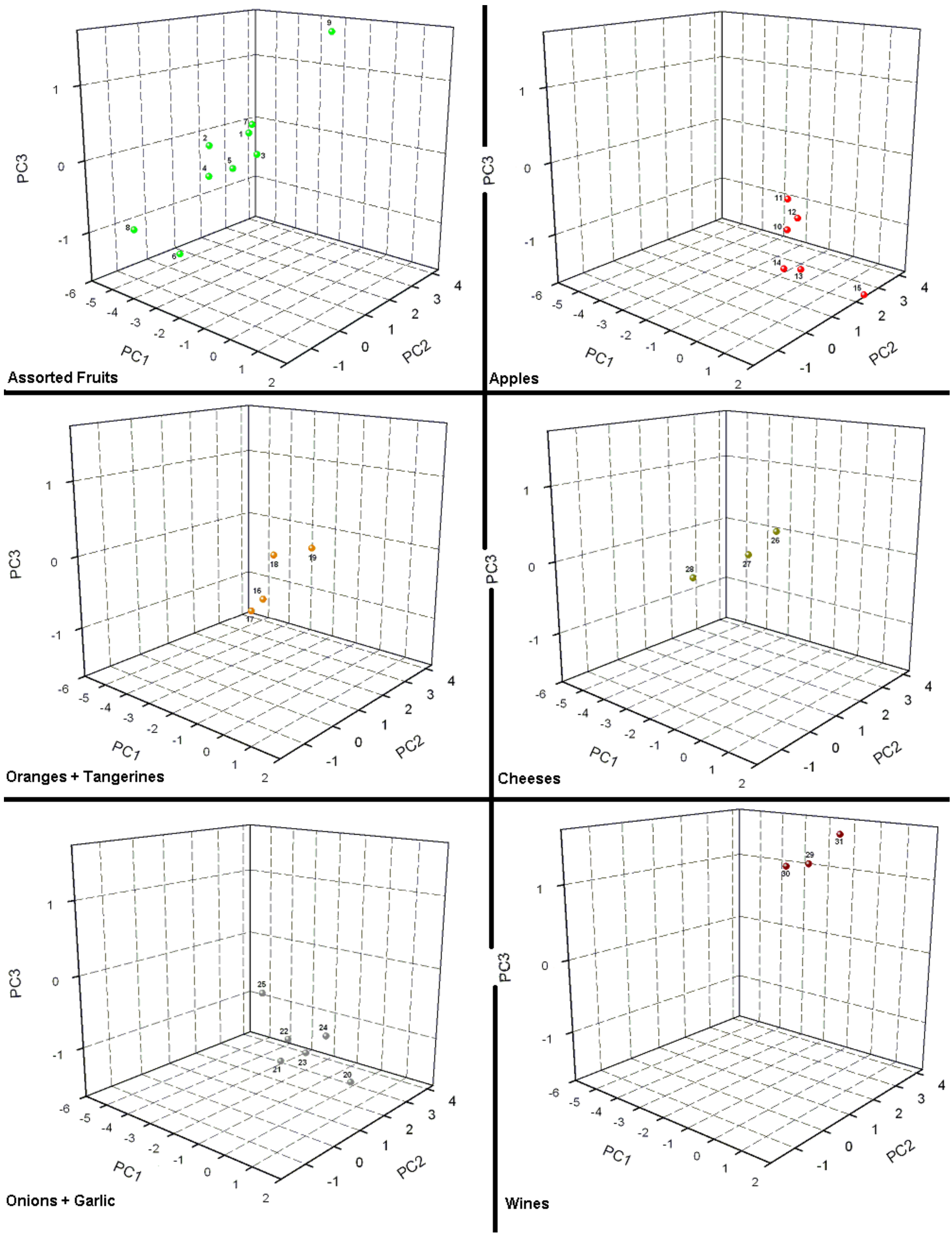

Fig. 10. PCA plot for food data. 1-Kiwi, 2-Mango, 3-Papaya, 4-Pineapple, 5-Strawberry, 6-Honeydew, 7-Cantaloupe, 8-Watermelon, 9-Red grape, 10-Ambrosia Apple, 11-Red Delicious Apple, 12-Granny Smith Apple, 13-Rome Apple, 14-Jazzenza Apple, 15-Gala Apple, 16-Navel Orange1, 17-Tangerine1, 18-Tangerine2, 19-Navel Orange2, 20-Red Onion, 21-Yellow Onion, 22-White Onion, 23-Garlic outer shell, 24-Garlic inner shell, 25-Garlic core, 26-Sharp Cheddar Cheese, 27-Swiss Cheese, 28-American Cheese, 29-White Merlot Wine, 30-White Zinfandel Wine, and 31-Pinot Grigio Wine.

The foods data was best presented in 3-dimensional PCA graphs, and shows food groupings in the PCA variable space that seem intuitive when the food names are revealed. The oranges and tangerines were adjacent to, but do not overlap the other assorted fruits and apples. The onions were adjacent to, and slightly overlapped the apples. The one outlying apple data point (15) was from a Gala apple that was stale, unlike the other five apples that were measured. Out of all the assorted fruits, the outlying red grape (9) was closest to the wine cluster, which makes sense since as these wines were made from grapes.

6. Conclusions

The nanocrystalline-thin film ITO-QCM sensors detected odors of various foods, producing data which allowed PCA analysis to group the foods in ways that seems intuitive. The ITO (as a thin film sensor), and the QCM (as a transducer) combined to show change in frequency responses and surface resistances as a function of time for each odor tested. PCA analysis showed selectivity for each group of odors. Further odor testing using ITO-QCM sensors and PCA analysis is in progress.

Acknowledgement

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually.

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Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

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