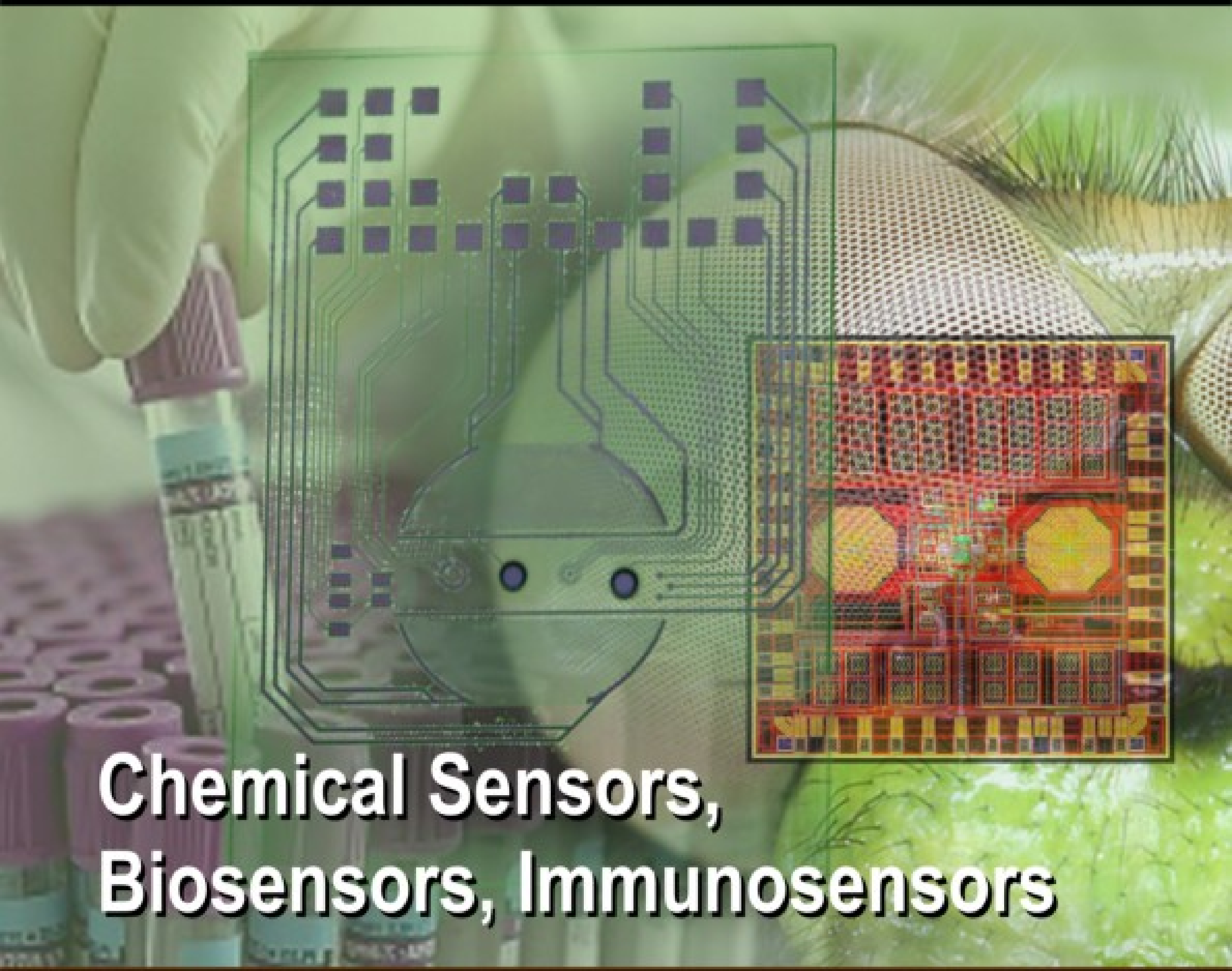
ISSN 1726-5479

SENSORS & TRANSDUCERS

vol. 113
2/10



Chemical Sensors, Biosensors, Immunosensors

International Frequency Sensor Association Publishing
IFSA

Sensors & Transducers

Volume 113, Issue 2,
February 2010

www.sensorsportal.com

ISSN 1726-5479

Editors-in-Chief: professor Sergey Y. Yurish, tel.: +34 696067716, fax: +34 93 4011989, e-mail: editor@sensorsportal.com

Editors for Western Europe
Meijer, Gerard C.M., Delft University of Technology, The Netherlands
Ferrari, Vittorio, Universitá di Brescia, Italy

Editor South America
Costa-Felix, Rodrigo, Inmetro, Brazil

Editor for Eastern Europe
Sachenko, Anatoly, Ternopil State Economic University, Ukraine

Editors for North America
Datskos, Panos G., Oak Ridge National Laboratory, USA
Fabien, J. Josse, Marquette University, USA
Katz, Evgeny, Clarkson University, USA

Editor for Asia
Ohyama, Shinji, Tokyo Institute of Technology, Japan

Editor for Asia-Pacific
Mukhopadhyay, Subhas, Massey University, New Zealand

Editorial Advisory Board

Abdul Rahim, Ruzairi, Universiti Teknologi, Malaysia
Ahmad, Mohd Noor, Nothern University of Engineering, Malaysia
Annamalai, Karthigeyan, National Institute of Advanced Industrial Science and Technology, Japan
Arcega, Francisco, University of Zaragoza, Spain
Arguel, Philippe, CNRS, France
Ahn, Jae-Pyoung, Korea Institute of Science and Technology, Korea
Arndt, Michael, Robert Bosch GmbH, Germany
Ascoli, Giorgio, George Mason University, USA
Atalay, Selcuk, Inonu University, Turkey
Atghiaee, Ahmad, University of Tehran, Iran
Augutis, Vygantas, Kaunas University of Technology, Lithuania
Avachit, Patil Lalchand, North Maharashtra University, India
Ayesh, Aladdin, De Montfort University, UK
Bahreyni, Behraad, University of Manitoba, Canada
Baliga, Shankar, B., General Monitors Transnational, USA
Baoxian, Ye, Zhengzhou University, China
Barford, Lee, Agilent Laboratories, USA
Barlingay, Ravindra, RF Arrays Systems, India
Basu, Sukumar, Jadavpur University, India
Beck, Stephen, University of Sheffield, UK
Ben Bouzid, Sihem, Institut National de Recherche Scientifique, Tunisia
Benachaiba, Chellali, Universitaire de Bechar, Algeria
Binnie, T. David, Napier University, UK
Bischoff, Gerlinde, Inst. Analytical Chemistry, Germany
Bodas, Dhananjay, IMTEK, Germany
Borges Carval, Nuno, Universidade de Aveiro, Portugal
Bousbia-Salah, Mounir, University of Annaba, Algeria
Bouvet, Marcel, CNRS – UPMC, France
Brudzewski, Kazimierz, Warsaw University of Technology, Poland
Cai, Chenxin, Nanjing Normal University, China
Cai, Qingyun, Hunan University, China
Campanella, Luigi, University La Sapienza, Italy
Carvalho, Vitor, Minho University, Portugal
Cecelja, Franjo, Brunel University, London, UK
Cerda Belmonte, Judith, Imperial College London, UK
Chakrabarty, Chandan Kumar, Universiti Tenaga Nasional, Malaysia
Chakravorty, Dipankar, Association for the Cultivation of Science, India
Changhai, Ru, Harbin Engineering University, China
Chaudhari, Gajanan, Shri Shivaji Science College, India
Chavali, Murthy, VIT University, Tamil Nadu, India
Chen, Jiming, Zhejiang University, China
Chen, Rongshun, National Tsing Hua University, Taiwan
Cheng, Kuo-Sheng, National Cheng Kung University, Taiwan
Chiang, Jeffrey (Cheng-Ta), Industrial Technol. Research Institute, Taiwan
Chiriac, Horia, National Institute of Research and Development, Romania
Chowdhuri, Arijit, University of Delhi, India
Chung, Wen-Yaw, Chung Yuan Christian University, Taiwan
Corres, Jesus, Universidad Publica de Navarra, Spain
Cortes, Camilo A., Universidad Nacional de Colombia, Colombia
Courtois, Christian, Universite de Valenciennes, France
Cusano, Andrea, University of Sannio, Italy
D'Amico, Arnaldo, Università di Tor Vergata, Italy
De Stefano, Luca, Institute for Microelectronics and Microsystem, Italy
Deshmukh, Kiran, Shri Shivaji Mahavidyalaya, Barshi, India
Dickert, Franz L., Vienna University, Austria
Dieguez, Angel, University of Barcelona, Spain
Dimitropoulos, Panos, University of Thessaly, Greece
Ding, Jianning, Jiangsu Polytechnic University, China
Kim, Min Young, Kyungpook National University, Korea South
Djordjevich, Alexandar, City University of Hong Kong, Hong Kong
Donato, Nicola, University of Messina, Italy
Donato, Patricio, Universidad de Mar del Plata, Argentina
Dong, Feng, Tianjin University, China
Drljaca, Predrag, Instersema Sensoric SA, Switzerland
Dubey, Venketesh, Bournemouth University, UK
Enderle, Stefan, Univ.of Ulm and KTB Mechatronics GmbH, Germany
Erdem, Gursan K. Arzum, Ege University, Turkey
Erkmen, Aydan M., Middle East Technical University, Turkey
Estelle, Patrice, Insa Rennes, France
Estrada, Horacio, University of North Carolina, USA
Faiz, Adil, INSA Lyon, France
Fericean, Sorin, Balluff GmbH, Germany
Fernandes, Joana M., University of Porto, Portugal
Francioso, Luca, CNR-IMM Institute for Microelectronics and Microsystems, Italy
Francis, Laurent, University Catholique de Louvain, Belgium
Fu, Weiling, South-Western Hospital, Chongqing, China
Gaura, Elena, Coventry University, UK
Geng, Yanfeng, China University of Petroleum, China
Gole, James, Georgia Institute of Technology, USA
Gong, Hao, National University of Singapore, Singapore
Gonzalez de la Rosa, Juan Jose, University of Cadiz, Spain
Granel, Annette, Goteborg University, Sweden
Graff, Mason, The University of Texas at Arlington, USA
Guan, Shan, Eastman Kodak, USA
Guillet, Bruno, University of Caen, France
Guo, Zhen, New Jersey Institute of Technology, USA
Gupta, Narendra Kumar, Napier University, UK
Hadjiloucas, Sillas, The University of Reading, UK
Haider, Mohammad R., Sonoma State University, USA
Hashsham, Syed, Michigan State University, USA
Hasni, Abdelhafid, Bechar University, Algeria
Hernandez, Alvaro, University of Alcala, Spain
Hernandez, Wilmar, Universidad Politecnica de Madrid, Spain
Homentcovschi, Dorel, SUNY Binghamton, USA
Horstman, Tom, U.S. Automation Group, LLC, USA
Hsiai, Tzung (John), University of Southern California, USA
Huang, Jeng-Sheng, Chung Yuan Christian University, Taiwan
Huang, Star, National Tsing Hua University, Taiwan
Huang, Wei, PSG Design Center, USA
Hui, David, University of New Orleans, USA
Jaffrezic-Renault, Nicole, Ecole Centrale de Lyon, France
Jaime Calvo-Galleg, Jaime, Universidad de Salamanca, Spain
James, Daniel, Griffith University, Australia
Janting, Jakob, DELTA Danish Electronics, Denmark
Jiang, Liudi, University of Southampton, UK
Jiang, Wei, University of Virginia, USA
Jiao, Zheng, Shanghai University, China
John, Joachim, IMEC, Belgium
Kalach, Andrew, Voronezh Institute of Ministry of Interior, Russia
Kang, Moonho, Sunmoon University, Korea South
Kaniusas, Eugenijus, Vienna University of Technology, Austria
Katake, Anup, Texas A&M University, USA
Kausel, Wilfried, University of Music, Vienna, Austria
Kavasoglu, Nese, Mugla University, Turkey
Ke, Cathy, Tyndall National Institute, Ireland
Khan, Asif, Aligarh Muslim University, Aligarh, India
Sapozhnikova, Ksenia, D.I.Mendeleyev Institute for Metrology, Russia
Saxena, Vibha, Bhbha Atomic Research Centre, Mumbai, India

Ko, Sang Choon, Electronics. and Telecom. Research Inst., Korea South
Kockar, Hakan, Balikesir University, Turkey
Kotulska, Malgorzata, Wroclaw University of Technology, Poland
Kratz, Henrik, Uppsala University, Sweden
Kumar, Arun, University of South Florida, USA
Kumar, Subodh, National Physical Laboratory, India
Kung, Chih-Hsien, Chang-Jung Christian University, Taiwan
Lacnjevac, Caslav, University of Belgrade, Serbia
Lay-Ekuakille, Aime, University of Lecce, Italy
Lee, Jang Myung, Pusan National University, Korea South
Lee, Jun Su, Amkor Technology, Inc. South Korea
Lei, Hua, National Starch and Chemical Company, USA
Li, Genxi, Nanjing University, China
Li, Hui, Shanghai Jiaotong University, China
Li, Xian-Fang, Central South University, China
Liang, Yuanchang, University of Washington, USA
Liawruangrath, Saisunee, Chiang Mai University, Thailand
Liew, Kim Meow, City University of Hong Kong, Hong Kong
Lin, Hermann, National Kaohsiung University, Taiwan
Lin, Paul, Cleveland State University, USA
Linderholm, Pontus, EPFL - Microsystems Laboratory, Switzerland
Liu, Aihua, University of Oklahoma, USA
Liu Changgeng, Louisiana State University, USA
Liu, Cheng-Hsien, National Tsing Hua University, Taiwan
Liu, Songqin, Southeast University, China
Lodeiro, Carlos, University of Vigo, Spain
Lorenzo, Maria Encarnacio, Universidad Autonoma de Madrid, Spain
Lukaszewicz, Jerzy Pawel, Nicholas Copernicus University, Poland
Ma, Zhanfang, Northeast Normal University, China
Majstorovic, Vidosav, University of Belgrade, Serbia
Marquez, Alfredo, Centro de Investigacion en Materiales Avanzados, Mexico
Matay, Ladislav, Slovak Academy of Sciences, Slovakia
Mathur, Prafull, National Physical Laboratory, India
Maurya, D.K., Institute of Materials Research and Engineering, Singapore
Mekid, Samir, University of Manchester, UK
Melnyk, Ivan, Photon Control Inc., Canada
Mendes, Paulo, University of Minho, Portugal
Mennell, Julie, Northumbria University, UK
Mi, Bin, Boston Scientific Corporation, USA
Minas, Graca, University of Minho, Portugal
Moghavvemi, Mahmoud, University of Malaya, Malaysia
Mohammadi, Mohammad-Reza, University of Cambridge, UK
Molina Flores, Esteban, Benemérita Universidad Autónoma de Puebla, Mexico
Moradi, Majid, University of Kerman, Iran
Morello, Rosario, University "Mediterranea" of Reggio Calabria, Italy
Mounir, Ben Ali, University of Sousse, Tunisia
Mulla, Imtiaz Sirajuddin, National Chemical Laboratory, Pune, India
Neelamegam, Periasamy, Sastra Deemed University, India
Neshkova, Milka, Bulgarian Academy of Sciences, Bulgaria
Oberhammer, Joachim, Royal Institute of Technology, Sweden
Ould Lahoucine, Cherif, University of Guelma, Algeria
Pamidighanta, Sayanu, Bharat Electronics Limited (BEL), India
Pan, Jisheng, Institute of Materials Research & Engineering, Singapore
Park, Joon-Shik, Korea Electronics Technology Institute, Korea South
Penza, Michele, ENEA C.R., Italy
Pereira, Jose Miguel, Instituto Politecnico de Setebal, Portugal
Petsev, Dimiter, University of New Mexico, USA
Pogacnik, Lea, University of Ljubljana, Slovenia
Post, Michael, National Research Council, Canada
Prance, Robert, University of Sussex, UK
Prasad, Ambika, Gulbarga University, India
Prateepasen, Asa, Kingmoungut's University of Technology, Thailand
Pullini, Daniele, Centro Ricerche FIAT, Italy
Pumera, Martin, National Institute for Materials Science, Japan
Radhakrishnan, S. National Chemical Laboratory, Pune, India
Rajanna, K., Indian Institute of Science, India
Ramadan, Qasem, Institute of Microelectronics, Singapore
Rao, Basuthkar, Tata Inst. of Fundamental Research, India
Raoof, Kosai, Joseph Fourier University of Grenoble, France
Reig, Candid, University of Valencia, Spain
Restivo, Maria Teresa, University of Porto, Portugal
Robert, Michel, University Henri Poincare, France
Rezazadeh, Ghader, Urmia University, Iran
Royo, Santiago, Universitat Politecnica de Catalunya, Spain
Rodriguez, Angel, Universidad Politecnica de Cataluna, Spain
Rothberg, Steve, Loughborough University, UK
Sadana, Ajit, University of Mississippi, USA
Sadeghian Marnani, Hamed, TU Delft, The Netherlands
Sandacci, Serghei, Sensor Technology Ltd., UK
Schneider, John K., Ultra-Scan Corporation, USA
Seif, Selemani, Alabama A & M University, USA
Seifter, Achim, Los Alamos National Laboratory, USA
Sengupta, Deepak, Advance Bio-Photonics, India
Shearwood, Christopher, Nanyang Technological University, Singapore
Shin, Kyuho, Samsung Advanced Institute of Technology, Korea
Shmaliy, Yuriy, Kharkiv National Univ. of Radio Electronics, Ukraine
Silva Girao, Pedro, Technical University of Lisbon, Portugal
Singh, V. R., National Physical Laboratory, India
Slomovitz, Daniel, UTE, Uruguay
Smith, Martin, Open University, UK
Soleymanpour, Ahmad, Damghan Basic Science University, Iran
Somani, Prakash R., Centre for Materials for Electronics Technol., India
Srinivas, Talabattula, Indian Institute of Science, Bangalore, India
Srivastava, Arvind K., Northwestern University, USA
Stefan-van Staden, Raluca-Ioana, University of Pretoria, South Africa
Sumriddetchka, Sarun, National Electronics and Computer Technology Center, Thailand
Sun, Chengliang, Polytechnic University, Hong-Kong
Sun, Dongming, Jilin University, China
Sun, Junhua, Beijing University of Aeronautics and Astronautics, China
Sun, Zhiqiang, Central South University, China
Suri, C. Raman, Institute of Microbial Technology, India
Sysoev, Victor, Saratov State Technical University, Russia
Szewczyk, Roman, Industrial Research Inst. for Automation and Measurement, Poland
Tan, Ooi Kiang, Nanyang Technological University, Singapore,
Tang, Dianping, Southwest University, China
Tang, Jaw-Luen, National Chung Cheng University, Taiwan
Teker, Kasif, Frostburg State University, USA
Thumbavanam Pad, Kartik, Carnegie Mellon University, USA
Tian, Gui Yun, University of Newcastle, UK
Tsiantos, Vassilios, Technological Educational Institute of Kaval, Greece
Tsigara, Anna, National Hellenic Research Foundation, Greece
Twomey, Karen, University College Cork, Ireland
Valente, Antonio, University, Vila Real, - U.T.A.D., Portugal
Vaseashta, Ashok, Marshall University, USA
Vazquez, Carmen, Carlos III University in Madrid, Spain
Vieira, Manuela, Instituto Superior de Engenharia de Lisboa, Portugal
Vigna, Benedetto, STMicroelectronics, Italy
Vrba, Radimir, Brno University of Technology, Czech Republic
Wandelt, Barbara, Technical University of Lodz, Poland
Wang, Jiangping, Xi'an Shiyou University, China
Wang, Kedong, Beihang University, China
Wang, Liang, Advanced Micro Devices, USA
Wang, Mi, University of Leeds, UK
Wang, Shinn-Fwu, Ching Yun University, Taiwan
Wang, Wei-Chih, University of Washington, USA
Wang, Wensheng, University of Pennsylvania, USA
Watson, Steven, Center for NanoSpace Technologies Inc., USA
Weiping, Yan, Dalian University of Technology, China
Wells, Stephen, Southern Company Services, USA
Wolkenberg, Andrzej, Institute of Electron Technology, Poland
Woods, R. Clive, Louisiana State University, USA
Wu, DerHo, National Pingtung Univ. of Science and Technology, Taiwan
Wu, Zhaoyang, Hunan University, China
Xiu Tao, Ge, Chuzhou University, China
Xu, Lisheng, The Chinese University of Hong Kong, Hong Kong
Xu, Tao, University of California, Irvine, USA
Yang, Dongfang, National Research Council, Canada
Yang, Wuqiang, The University of Manchester, UK
Yang, Xiaoling, University of Georgia, Athens, GA, USA
Yaping Dan, Harvard University, USA
Ymeti, Aurel, University of Twente, Netherland
Yong Zhao, Northeastern University, China
Yu, Haihu, Wuhan University of Technology, China
Yuan, Yong, Massey University, New Zealand
Yufera Garcia, Alberto, Seville University, Spain
Zakaria, Zulkarnay, University Malaysia Perlis, Malaysia
Zagnoni, Michele, University of Southampton, UK
Zamani, Cyrus, Universitat de Barcelona, Spain
Zeni, Luigi, Second University of Naples, Italy
Zhang, Minglong, Shanghai University, China
Zhang, Qintao, University of California at Berkeley, USA
Zhang, Weiping, Shanghai Jiao Tong University, China
Zhang, Wenming, Shanghai Jiao Tong University, China
Zhang, Xueji, World Precision Instruments, Inc., USA
Zhong, Haoxiang, Henan Normal University, China
Zhu, Qing, Fujifilm Dimatix, Inc., USA
Zorzano, Luis, Universidad de La Rioja, Spain
Zourob, Mohammed, University of Cambridge, UK

Sensors & Transducers Journal (ISSN 1726-5479) is a peer review international journal published monthly online by International Frequency Sensor Association (IFSA).
Available in electronic and on CD. Copyright © 2009 by International Frequency Sensor Association. All rights reserved.

Sensors & Transducers Journal

Contents

Volume 113
Issue 2
February 2010

www.sensorsportal.com

ISSN 1726-5479

Research Articles

Authors are encouraged to submit article in MS Word (doc) and Acrobat (pdf) formats by e-mail: editor@sensorsportal.com
Please visit journal's webpage with preparation instructions: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm

International Frequency Sensor Association (IFSA).

Sensors & Transducers Journal, Vol. 113, Issue 2, February 2010, pp. 71-81

Sensors & Transducers

ISSN 1726-5479

http://www.sensorsportal.com

The Use of Calixarene Thin Films in the Sensor Array for VOCs Detection and Olfactory Navigation

Alan F. Holloway, Alexei Nabok, *Abbass A. Hashim, Jacques Penders
Sheffield Hallam University, Materials and Engineering Research Institute,
Sheffield, S1 1WB, UK
Tel: 441142253682, fax: 441142253433
E-mail: a.hashim@shu.ac.uk

Received: 19 January 2010 /Accepted: 19 February 2010 /Published: 26 February 2010

Abstract: This work is dedicated to the development of a sensor array for detection of volatile organic chemicals (VOCs) in pre-explosive concentrations as well as for olfactory robotic navigation in the frame of two EU projects. A QCM (quartz crystal microbalance) sensor array was built utilising quartz crystals spun-coated with thin films of different amphiphilic calixarene molecules to provide a base for pattern recognition of different volatile organic chemicals (VOCs). Commercial Metal-oxide semiconductor (MOS) sensors were also used in the same array for the benefit of comparison. The sensor array was tested with a range of organic vapours, such as hydrocarbons, alcohols, ketones, aromatics, etc, in concentrations below LEL and up to UEL (standing for lower and upper explosion limit, respectively); the sensor array proved to be capable of identification and concentration evaluation of a range of VOCs. Comparison of QCM and MOS sensors responses to VOCs in the LEL-UEL range showed the advantage of the former. In addition, the sensor array was tested on the vapours of camphor from cinnamon oil in order to prove the concept of using the "scent marks" for robotic navigation. The results showed that the response signature of QCM coated with calixarenes to camphor is very much different from those of any other VOCs used. Adsorption and de-sorption rates of camphor are also much slower comparing to VOCs due to a high viscosity of the compound. Our experiments demonstrated the suitability of calixarene sensor array for the task and justified the use of camphor as a "scent mark" for olfactory navigation. *Copyright © 2010 IFSA.*

Keywords: QCM & MOS sensors, VOCs, Pattern recognition, ANN, Olfactory navigation

---

1. Introduction

Detection of volatile organic chemicals (VOCs) in high concentrations is a very important problem of Health and Safety. The presence of VOCs is concentrations between LEL and UEL may cause fire or/and explosion triggered by an accidental electrical spark. There were several incidences of that type recorded recently; and this stimulates great demands on VOC sensors. The most common and commercially available nondispersive infrared (NDIR) sensors are based on detection of characteristic infrared spectral characteristics of VOCs [1]; these sensors are quite complex and relatively expensive. At the same time the research in calixarene thin film films carried out in recent years revealed their unique properties of fast and fully reversible adsorption of VOCs in high concentrations close to the saturated vapour pressures [2, 3]. The concentration range fits very well into LEL-UEL band. The mechanism of capillary condensation of VOCs in nanoporous structure of thin films of amphiphilic calixarene derivatives was suggested to explain the observed behaviour [4]. Further research work was focused on the utilisation of quartz crystal microbalance (QCM) coated with calixarenes for detection of VOCs and has resulted in the development of prototype VOCs sensor devices. Although the selectivity of particular calixarene derivatives to VOCs is rather poor, the recognition of VOCs can be achieved with QCM impedance measurements [5, 6] or QCMD method [7, 8]. An alternative way of VOCs indentification lies in the use of array of QCM sensors coated with different calixarene derivatives [9]. The revival of interest to the subject of VOC detection was stimulated by European research programme in robotics focused on the use of mobile robots to assist search and rescue operations in potentially hazardous environments where, under normal circumstances human presence would be risky. The chemical sensor array is designed to be mounted on the mobile robotic platform. The data obtained will be used for both gas detection (monitoring) and olfactory based navigation – localizing the source of the potential hazard and also to provide route planning information.

This work is therefore dedicated to the development of an array of quartz crystals coated with different calixarenes and its testing to a range of VOCs of different concentrations in LEL-UEL range. Another aspect of the work is related to realization of the principles of olfactory navigation for mobile robots [10]. It has been suggested that robots can follow “scent marks” using the sensor array approach. Previous attempts in this direction were made with the use of metal oxide semiconductor (MOS) sensors [10] and different scent marks including camphor [11]. The choice of camphor essential oil was justified by unique “smell signature” of this compound as compared to other VOCs, as well as by its slow evaporation rate which makes the scent marks last longer. From our point of view, QCM sensors are more suitable for detection of camphor. Therefore, several tests of a coated QCM-calixarene sensor array on camphor were performed aiming at realization of the robotics olfactory navigation in future.

2. Sensor Array Design and Measurements Routine

A sensor array shown in Fig. 1 contains eight QCM sensors coated with different calixarene derivatives (one uncoated quartz crystal is used as reference). In addition, six commercial MOS sensors (Figaro Engineering Inc) are introduced for the benefit of comparison as well as for detection of other gases, such as oxygen, carbon monoxide, natural gas, cyanide gas, etc. Analysis of other gases however is beyond the task of this work which is focused entirely on detection of VOCs. All sensors were assembled in the PTFE circular chamber with inlet and outlet tubes for gases (vapours) injection and flushing with fresh air, respectively.

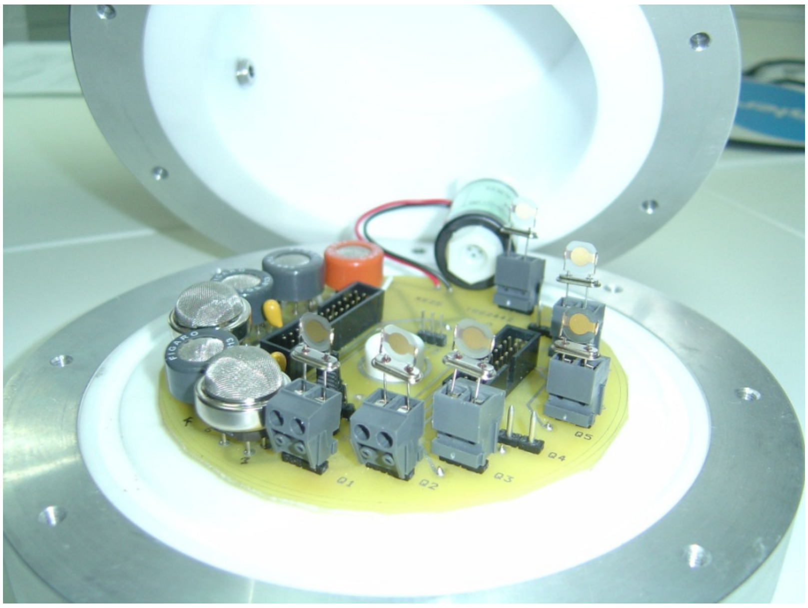


Fig. 1. The view of the QCM/MOS gas sensor array.

The secondary electronics, i.e. oscillation circuits for QCM, power supplies for MOS and multiplexers have been designed and fabricated in house. The crystal driver circuits are based on a Pierce oscillator using a standard Texas Instruments crystal oscillator driver integrated circuit. The outputs of which are fed into an 8 channel computer controlled relay multiplexer; subsequently an Agilent frequency counter measures the resonant frequency of each crystal. The MOS devices simply form part of a potential divider network and the output voltages are sampled using a 12 Bit ADC at 1 second intervals. All MOS measurements are controlled via an embedded microcontroller.

All the secondary electronics reside outside the exposure chamber with only the sensing elements exposed to the analytes inside the PTFE cell. All sensors are connected to a PC using an RS232 interface with the overall data acquisition performed through a LabView program which collects the readings from 14 channels corresponding to the QCM and MOS sensors. All further data processing is performed within the LabView software.

The following amphiphilic calixarene molecules were used in this work: (i) a range of calix[4]resorcinarenes having substituting alkyl chains of different length, e.g. $C_{17}H_{35}$, $C_{15}H_{31}$, $C_{11}H_{23}$, C_5H_{11}, and CH_3 named, respectively, as C4RA-C17, C4RA-C15, C4RA-C11, C4RA-C5, and C4RA-C1; (ii) tetra-tertbutyl calix[4]arene; and (iii) sexta-tertbutyl calix[6]arene. The above calixarene derivatives, chemical structure of which are shown in Fig. 2, have different size of inner cavities and therefore provide a base for pattern recognition of different VOCs. The above calixarene derivatives were synthesised at Sheffield University, UK and in the Institute of Organic Chemistry, Academy of Sciences of Ukraine. Thin films of all calixarenes were deposited on AT-cut quartz crystals (Euroquartz Limited) by spin coating using the Electronic Microsystems model 4000 spinner. A special holder for quartz crystals has been designed in-house. The spin speed was selected as 2000 rpm. All compounds were dissolved in ethanol in concentrations of 15 mg/ml. The deposition parameters were optimised in order to achieve the required film thickness and good homogeneity [5, 6]. The quartz crystals were numbered as follows: crystals Q1, Q2, Q3, Q4, and Q5 were coated with C4RA molecules having C17, C15, C11, C5, and C1 alkyl chains, respectively; Q6 and Q7 were coated with ttb-C4A and ttb-C6A, respectively.

The thickness of films deposited on silicon substrates was controlled with ellipsometry. J.A. Woollam M2000V spectroscopic ellipsometer was used for this purpose. Typical values of thickness were in the range of 320 nm. Similar thickness values were obtained by comparison of the oscillation frequency of quartz crystals before and after coating using Sauerbrey equation [12]. The homogeneity of calixarene coatings on silicon substrates was checked with AFM using Nanoscope IIIa instrument (Digital Technology) operating in tapping mode with Veeco tips of 4 to 7nm in radius. Typical AFM images shown in Fig. 3a demonstrate a smooth surface for majority of calixarene films with the mean roughness of around 0.4-0.45 nm; the films of C4RA-C1 however contain pin-holes which have little impact on QCM measurements. The film thickness of around 300 nm can be estimated from the depth of the scratch on the AFM image in Fig. 3b.

The sensor array was tested with a wide range of vapours, produced by organic solvents from different classes, namely hexane (hydrocarbons), n-propanol (alcohols), benzene, toluene, m-xylene (aromatic), acetone (ketones), chroloform (chloro-hydrocarbons). All the solvents of high purity were purchased from Aldrich, UK. In order to achieve the required vapour concentration, the respective liquid solvents were injected into the chamber with a micro-syringe. The injected amount of liquid solvents was varied from 0.1 µl to 50 µl depending on the type of solvent.

The respective vapour concentrations in *ppm* units were calculated using known data, such as molecular weight (M), density (ρ), for all solvents used:

$$C(ppm) = \frac{\rho \times Q_S \times 22.4 \times 1000}{M \times V}, \tag{1}$$

where Q_S is the quantity of liquid solvent in µl, V is the volume of the gas cell, and 22.4 is the molar gas volume constant. The relation between vapour concentrations measured in (*ppm*) and (*g/l*) is established as:

$$C(ppm) = \frac{C(g/l) \times R_g \times T}{M}, \tag{2}$$

where $R_g = 8.206 \cdot 10^{-2}$ ($l \cdot atm \cdot K^{-1} mol^{-1}$) is the gas constant, T is the temperature in degrees Kelvin.

Sometimes it is useful to express the concentration in the units of pressure relative to the saturated vapour pressure (*P/Ps*); this is particularly the case for capillary condensation of vapours in calixarene films [4]. The values of the saturated vapour pressure are known parameters for all the solvents used are presented in Table 1. The vapour pressure in atmospheres ($atm = \frac{kPa}{101.325}$) can be calculated from the respective concentration as:

$$P(atm) = \frac{C(g/l) \times M \times V}{R_g \times T}, \tag{3}$$

where C is the concentration in grams per litre, M is the molecular weight of the solvent in grams, V is the volume of a cell. All physical parameters of the solvents used are summarized in the Table 1.

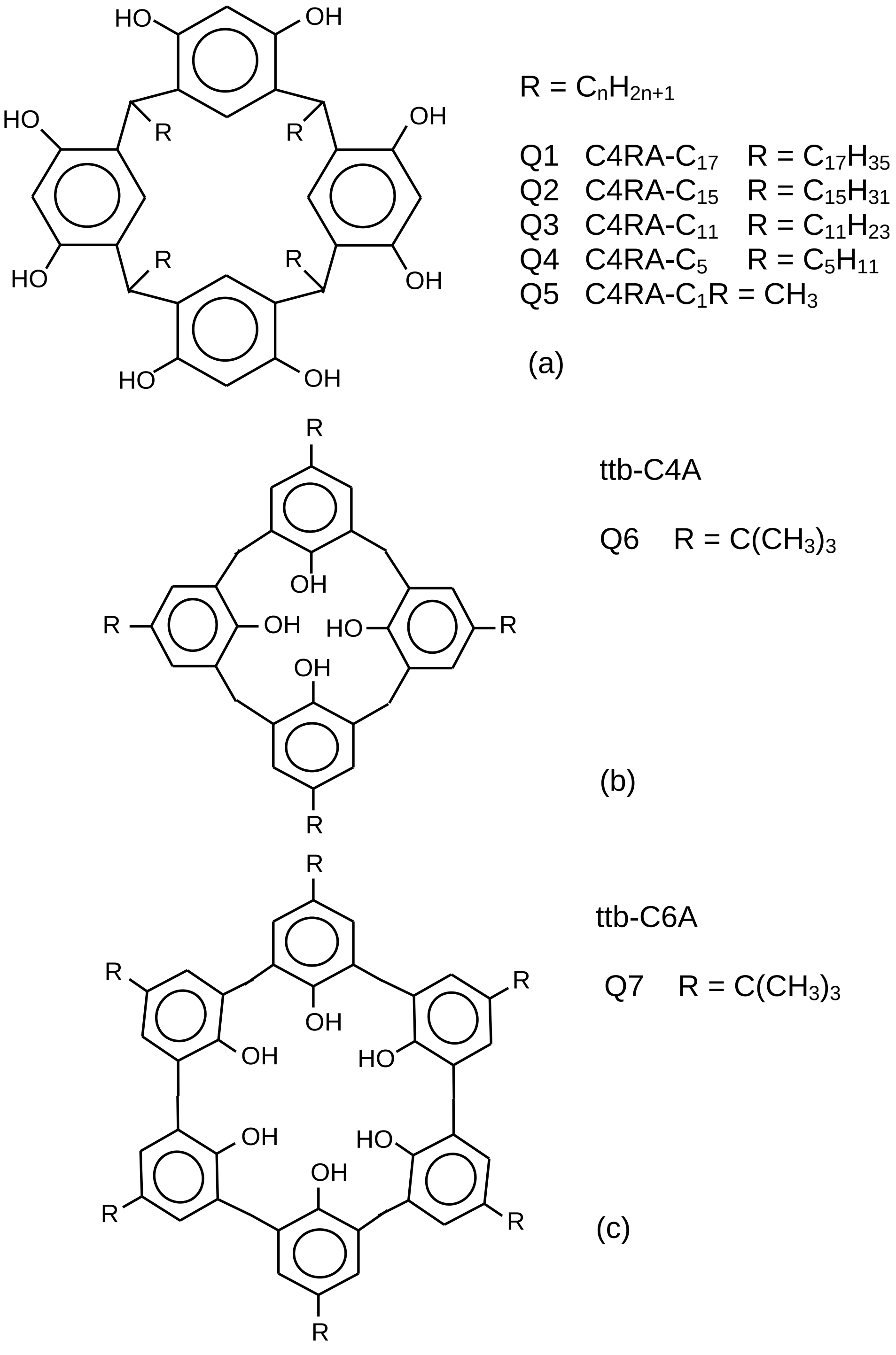
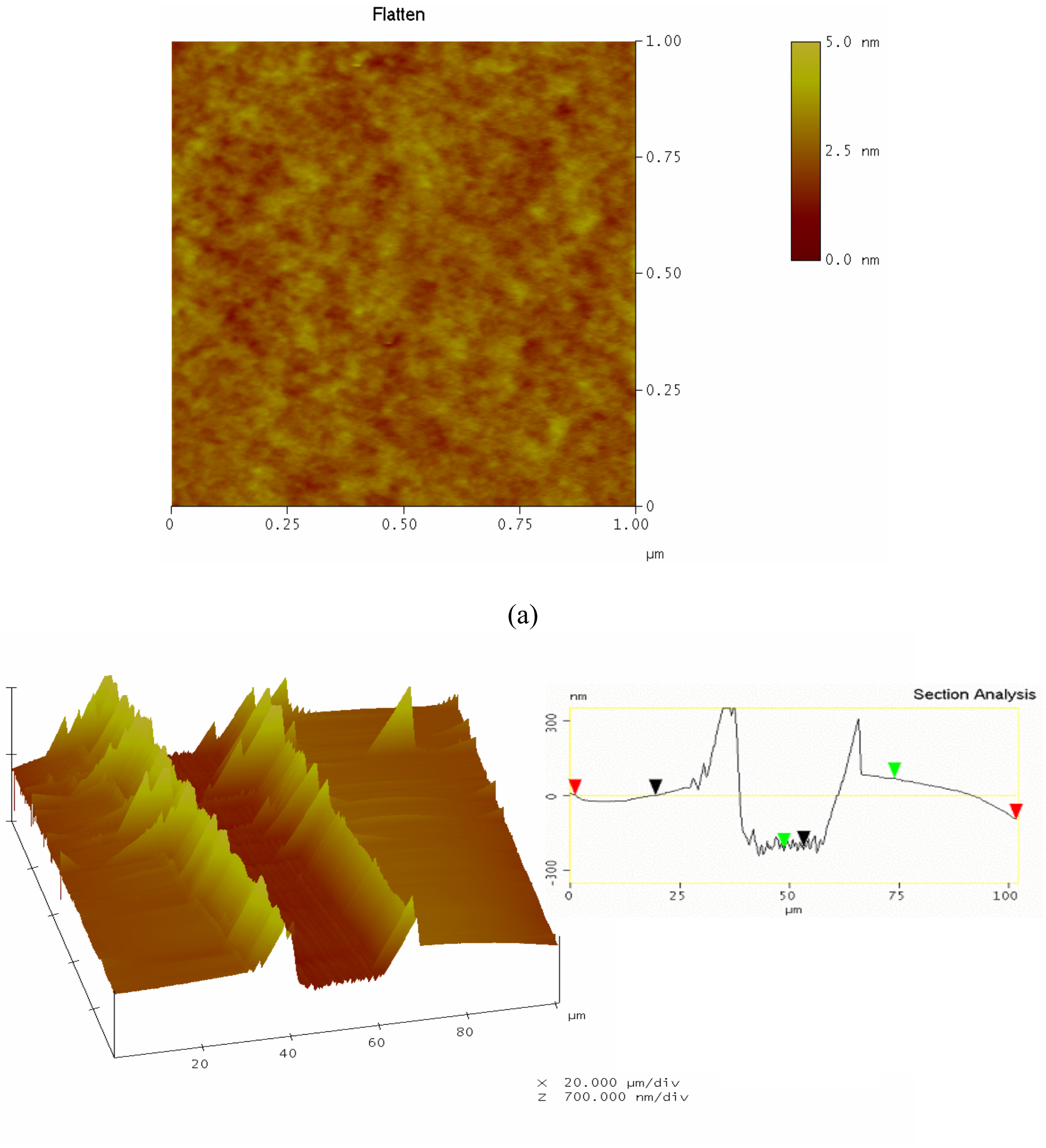


Fig. 2. Chemical structures of amphiphilic calixarene derivatives:
(a) calix[4]resorcinarenes (crystals Q1, Q2, Q3, Q4, and Q5);
(b) tetratertbutyl-calix[4]arene (crystal Q6);
(c) tetratertbutyl-calix[6]arene (crystal Q7)



(a)

(b)

Fig. 3. (a) Tapping mode AFM image of C4RA-C17 film on silicon. (b) Pseudo 3D image of the scratch on surface of C4RA-C17 with the section analysis.

Table 1. Physical parameters of selected VOCs.

Chemical	Molecular weight	Vapour pressure (kPa)	LEL (%)	UEL (%)	Saturated vapour concentration (ppm)
Benzene	78.11	10	1.2	7.8	98692.3
Hexane	86.2	17	1.1	7.5	167776.9
M - Xylene	106.2	0.8	1.1	7	7895.4
Acetone	58.1	24	2.5	12.8	236861.6
Propanol	60.09	2	2.2	13.7	19738.5
Pentane	72.15	65.1	1.5	7.8	642487
Chloroform	119.38	21.28	n/a	n/a	210017.3
Camphor	152.24	0.0867	0.6	3.5	855.2631579

In addition to the VOCs mentioned above, camphor essential oil from cinnamon was used to produce vapours of camphor. The values of M = 152.24, ρ=0.9091 g/cm^3 and Ps = 0.0867 kPa used were characteristics of pure camphor. The content of camphor in the essential oil is unknown unfortunately, so the obtained concentrations of camphor can be considered as a maximal estimate. The background effect of liquid oil on QCM was negligible as was confirmed by test measurements of vapours produced by refined neutral (odourless) vegetable oil.

4. Experimental Results and Analysis

Typical responses of QCM and MOS sensors to the injection of 9 µl of benzene are shown in Fig. 4. The sampling number in the horizontal axes in the graph corresponds to about 5 second periods. QCM sensor shows a decrease of the oscillation frequency of more than 100 Hz, while MOS sensor gives an increase in the conductivity measured through a change in voltage at the ADC input. As one can see, the MOS sensor responds very quickly (few seconds) but soon reaches the upper limit of detection although the vapour concentration of about 0.042 P/Ps is far away from saturated vapours. The recovery of MOS sensors is rather poor (about 70 % in 100 s); full recovery may take much longer (up to 30 min).

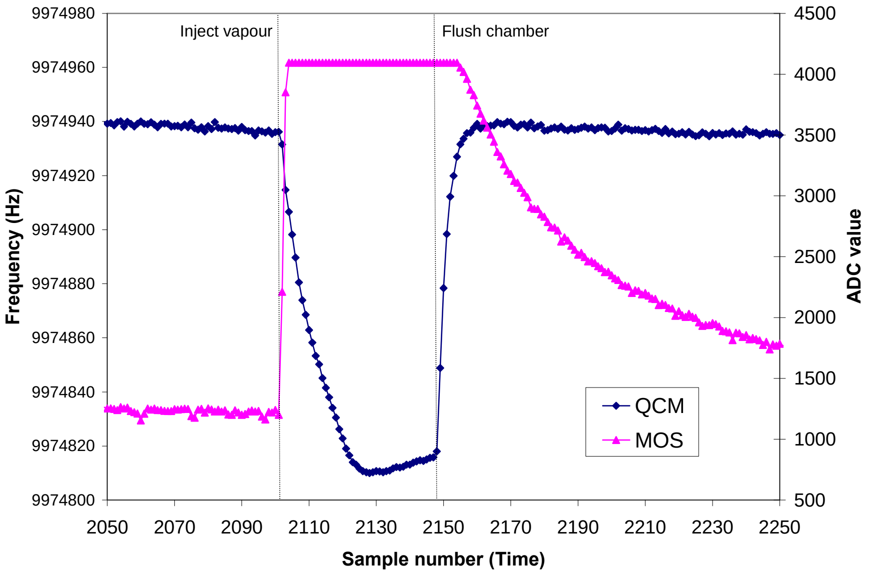


Fig. 4. Typical responses of QCM and MOS sensors to the injection of 1 *µl* of benzene into the cell.

QCM sensors responds slower than MOS ones but recover quicker. A relatively slow (120-150 s) response of QCM sensors is due to evaporation of liquid solvent in a large (0.55 *l*) chamber; our early experiments in smaller (50 ml) chamber showed much faster response in the range of 10-15 s [5-7]. Recovery is much faster (40-50 s) and complete, which is typical for thin LB/spun films amphiphilic calixarenes [5, 6]. Comparison of responses of QCM and MOS sensors clearly shows the advantages of the latter in detection of high concentrations of organic vapours. MOS sensors are simply not suitable because they saturate at much smaller concentrations.

The series of responses of all QCM sensors to different concentrations of propanol in Fig. 5 show an obvious correlation between the values of frequency change and the alkyl chain length of calixarene derivatives and the size of the calixarene cavity. Long alkyl chains C17, C15, and C11 in Q1, Q2, and Q3 yield large response than Q4 and particularly Q5 having shorter alkyl chain of C5 and C1. Q6 coated with ttb-C4A gives even smaller response; and Q7 coated with ttb-C6A is practically non-responding. Also the stability of operation of QCM Q1-Q4 is much better as compared to that for Q5-Q7 where a drift of the baseline frequency is observed. Longer alkyl chains provide better lipophilic interaction with molecules of organic solvents (propanol this time) and thus cause larger response. Also, calixarenes with longer alkyl chains form more porous films structure where the effect of capillary condensation is more pronounced as compared to more condensed films of calixarenes with shorter alkyl chains. The films of ttb-C6A molecules having the largest size of the cavity practically do not adsorb any of the analytes studied. The most likely reasons for that may be related to almost equal adsorption and desorption rates in such molecules or simply to much more dense film structure with no pores and therefore no capillary condensation.

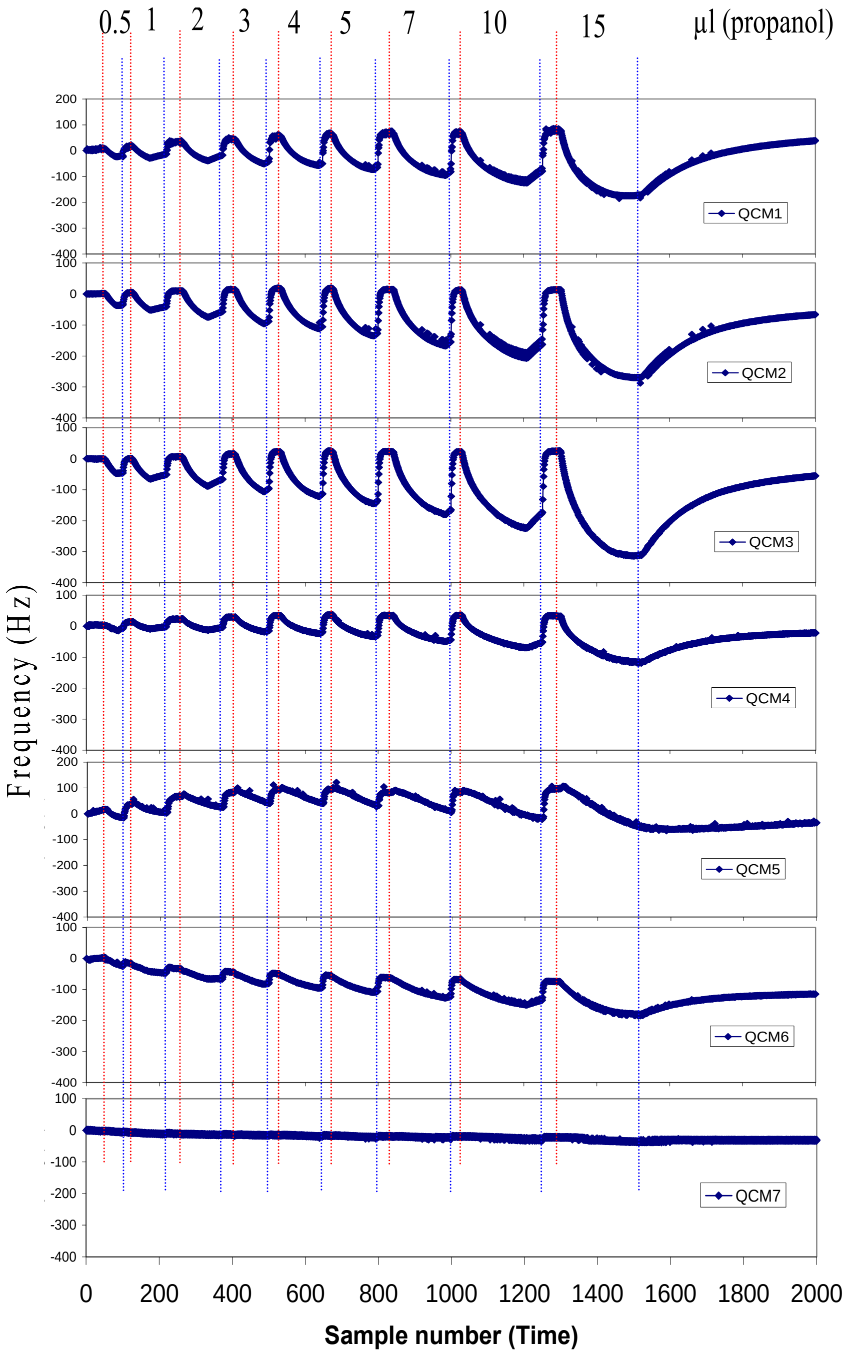


Fig. 5. The series of responses of quartz crysrals Q1 - Q7 to consequitive cycles of injections of liquid propanol / flushing with air with gradually increased amount of propanol from 0.1 to 15 µl. Red dotted lines correspond to the momemnt of injection, blue dotted lines – to flushing with air.

Concentration dependence of responses of all QCM to propanol vapour is shown in Fig. 6.

All the curves presented show the trend of saturation at the pressures close to the saturated vapour pressure. The highest response is recorded for Q3 (C4RA-C11) with slightly smaller responses of other long alkyl chain calixarenes: Q2 (C4RA-C15 and Q1 (C4RA-C17). It seems that C4RA-C11 molecules provide an optimal adsorption conditions for propanol. Calixarenes with shorter alkyl chains give much smaller response (see Q4, Q5, and Q6); Q7 coated with ttb-C6A does not respond practically. This trend is repeated for all the analytes studied with some deviations. The results are very much in line with the concept of capillary condensation [4], according to which calixarenes with long alkyl chains provides sufficient liphophilic interaction with the molecules of solvent and at the same time give larger pore size in thin films. In contrast, calixarenes with shorter alkyl chains provides more closely packed film structure with smaller pore size as well as a lower level of lipophilic interaction resulting in smaller responses.

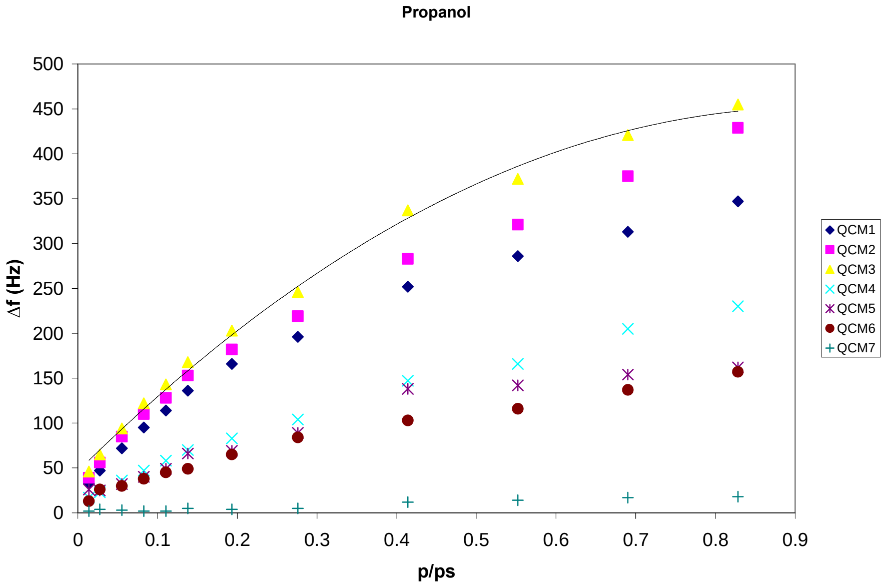


Fig. 6. Dependences of *Δf (Hz)* for all 7 crystals against vapour the relative pressure (*P/Ps*) of propanol vapours.

Fig. 7 shows the concentration dependences of the response of Q3 (C4RA-C11) to different analytes including camphor. The concentration is given in ppm units this time since the exact value of the saturated vapour pressure of camphor essential oil is not known. It can be noticed that less volatile VOCs give larger response because they produce much less vapour pressure at given concentration. For that reason, a very viscous camphor oil is standing alone from the rest of analytes. In fact, the actual vapour concentration of camphor can be even smaller. The calculations have been performed on the assumption of 100% pure camphor which is not the case. Because of that, the curve for the camphor can be even further away from the rest of analytes. The experimental data presented proved the suggestion that camphor produces characteristic signature smell different from the rest of common VOCs and therefore can be used as a "scent mark" for robotic navigation.

Recording of responses of QCM sensors coated with different calixarene derivatives to exposure of different VOCs in different concentrations aims at building a database for pattern recognition of VOCs. The diagram in Fig. 8 shows a comparison of responces of all QCM sensors to the vapours of propanol and m-xylene of 0.5 *P/Ps*. Apart from Q7 which does not practically respond, other crystals

Q1 -Q6 gives slightly different responces although the general trend of domination of Q1-Q3 is clear. These differences are enough for pattern recognition of VOCs in a 7-dimensional space of sensor responces, which can be done using approprate software, for example ANN (artificial neural network).

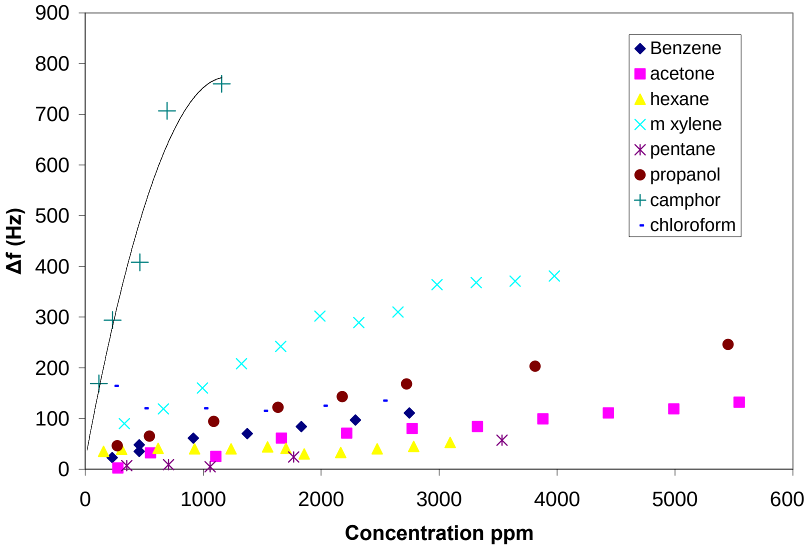


Fig. 7. Dependence of *Δf (Hz)* QCM 3 (C4RA-C11) against the concentration of different analytes in *ppm*.

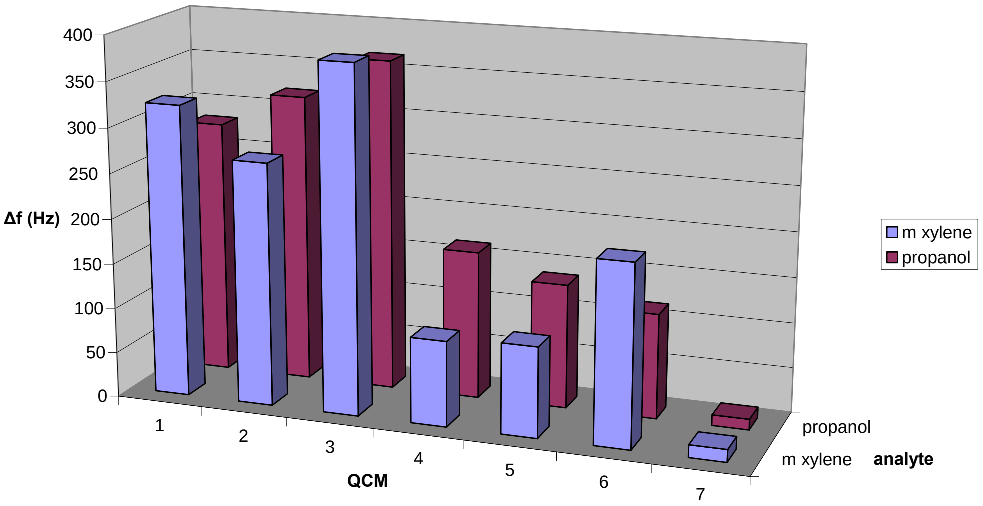


Fig. 8. The comparison of responses of QCM sensors Q1- Q7 to 0.5 *P/Ps* of propanol and m-xylene.

5. Conclusions

An array QCM and MOS sensors was build and tested on vapours of different VOCs. QCM sensors were found to be more suitable for detection of VOCs in high pre-explosive concentrations in the range of 10^3 -10^4 ppm, while MOS are more suitable for detection of VOCs in concentrations of at least two orders of magnitude lower, as well as for other gases such as oxygen, carbon monoxide, natural gas, cyanide gas, and many more.

The use of quartz crystals coated with different amphiphilic calixarene derivatives facilitates for pattern recognition of different VOCs. The experimental work of building a database for pattern recognition of VOCs is underway. The ANN is an obvious choice for further data analysis in order to identify and quantify various gases and vapours associated with fire. The complete sensor array installed on the mobile robotic platform will be used as for monitoring the concentration of VOCs and other toxic gases associated with fire as well as for robotic navigation.

Camphor was found to have a characteristic response pattern different from the rest of VOCs, and it can be used as a 'scent mark' for robotic navigation.

Acknowledgements

This work was supported by two EU projects IST-ViewFinder-045541 and IST-Guardians -045269.

References

[1]. Th. Lang, H.-D. Wiemhöfer and W. Göpel, Carbonate Based CO_2 Sensors with High Performance, *Sensors and Actuators B*, 34, 1996, pp. 383-387.

[2]. A. V. Nabok, N. V. Lavrik, Z. I. Kazantseva, B. A. Nesterenko, L. N. Markovskiy, V. I. Kalchenko, A. N. Shivaniuk, Complexing Properties of Calix[4]resorcinolarene LB Films, *Thin Solid Films,* 259, 1995, pp. 244-247.

[3]. A. Nabok, A. Hassan, A. K. Ray, O. Omar, V. Kalchenko, Study of adsorption of some organic molecules in calix[4]resorcinolarene LB films by surface plasmon resonance, *Sensors and Actuators B*, 45, 1997, pp. 115-121.

[4]. A. V. Nabok, A. K. Hassan, A. K. Ray, Condensation of organic vapours within Nanoporous Calixarene Thin Films, *Journal of Material Chemistry*, 10, 2000, pp. 189-194.

[5]. A. F. Holloway, A. Nabok, M. Thomson, A. K. Ray, D. Crowther, J. Siddiqi, New Method of Vapour Discrimination Using the Thickness Shear Mode (TSM) Resonator, *Sensors,* 3, 2003, pp. 170-174.

[6]. A. F. Holloway, A. Nabok, M. Thompson, A. K. Ray, T. Wilkop, Impedance analysis of the thickness shear mode resonator for organic vapour sensing, *Sensors & Actuators,* 99, 2004, pp. 355-360.

[7]. M. Rodahl, F. Hook, A. Krozer, P. Bzezinkski, and B. Kasemo, Quartz crystal microbalance setup for frequency and Q-factor measurements in gaseous and liquid environments, *Rev. Sci. Instrum.,* 66, 1995, pp. 3924-3930.

[8]. M. Rodahl and B. Kasemo, A simple setup to simultaneously measure the resonant frequency and the absolute dissipation factor of a quartz crystal microbalance, *Rev. Sci. Instrum*., 67, 1996, pp. 3238-3241.

[9]. A. Holloway, A. Nabok, M. Thompson, J. Siddiqi, A. Ray, Discriminative sensing, of volatile organic solvents. Comparative analysis using different QCM techniques, *Proc. IEEE Sensors 2004*, Vienna, 24-27 October, 1-3, 2004, pp. 1500-1503.

[10].L. Marques, U. Nunes, A. T. de Almeida, Olfaction-based mobile robotic navigation, *Thin Solid Films*, 418, 51, 2002.

[11].R. Russel, D. Thiel, A. Mackay-Sim, Sensing odor trails for mobile robot navigation, *Proc. of IEEE Conference on Robotics and Automation,* 1994, pp. 2672-2677.

[12].G Sauerbrey, Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung, *Zeitschrift für Physik*, 155, 1959, pp. 206.

Sensors & Transducers Journal

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. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

Topics Covered

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:

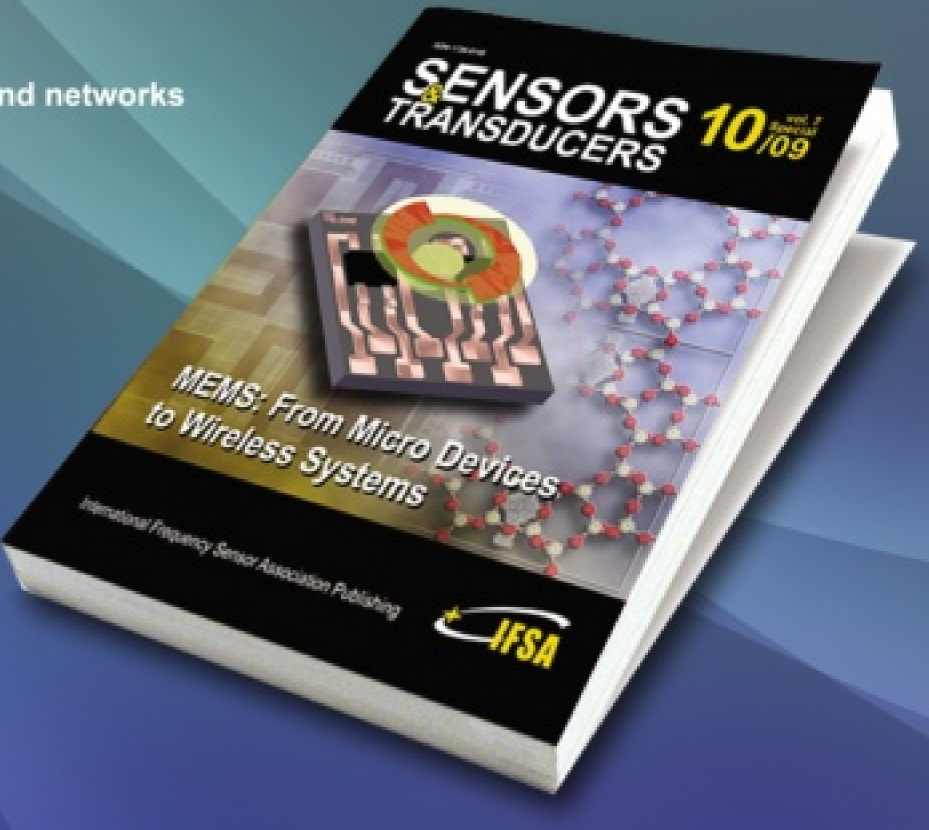
- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors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

Submission of papers

Articles should be written in English. Authors are invited to submit by e-mail editor@sensorsportal.com 8-14 pages article (including abstract, illustrations (color or grayscale), photos and references) in both: MS Word (doc) and Acrobat (pdf) formats. Detailed preparation instructions, paper example and template of manuscript are available from the journal's webpage: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm Authors must follow the instructions strictly when submitting their manuscripts.

Advertising Information

Advertising orders and enquires may be sent to sales@sensorsportal.com Please download also our media kit: http://www.sensorsportal.com/DOWNLOADS/Media_Kit_2009.pdf


SENSORS & TRANSDUCERS
10/09
MEMS: From Micro Devices to Wireless Systems
International Frequency Sensor Association Publishing
IFSA