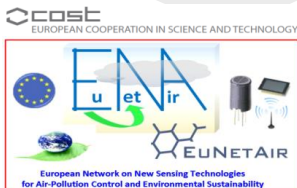




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COST Action TD1105
European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability - EuNetAir

**FIRST INTERNATIONAL WORKSHOP on
New Sensing Technologies and Transducers for Air-Quality Monitoring**

Barcelona, 20 June 2013

**Barcelona International Convention Centre (CCIB)
Plaça de Willy Brandt, 11-14, E- 08019 Barcelona, Spain**

| AGENDA | |
|--------------------------------|---|
| 20 June 2013 - Thursday | |
| 16:00 - 20:00 | REGISTRATION to COST Action Satellite WORKSHOP |
| 16:30 - 18:30 | COST Action Session 1 |
| 18:30 - 19:00 | <i>Break</i> |
| 18:30 - 19:00 | COST Action Poster Session |
| 19:00 - 20:00 | COST Action Session 2 |
| 20:00 - 20:10 | <i>Workshop Adjourns and Farewell</i> |

COST Action TD1105 EuNetAir

**OPEN SATELLITE WORKSHOP to
Transducers 2013 - Eurosensors XXVII**

The 17th International Conference
on Solid-State Sensors,
Actuators and Microsystems



**The 17th International Conference
on Solid-State Sensors,
Actuators and Microsystems
June 16-20, 2013, Barcelona, Spain**



Background and goals

About COST Action TD1105 EuNetAir

COST Action TD 1105 EuNetAir (www.cost.eunetair.it), a Concerted Action on *New Sensing Technologies for Air-Pollution Control and Environmental Sustainability*, is a running Networking funded in the framework *European Cooperation in the field of Scientific and Technical Research (COST)* during 2012-2016.

The main objective of the Concerted Action is to develop new sensing technologies for Air Quality Control at integrated and multidisciplinary scale by coordinated research on nanomaterials, sensor-systems, air-quality modelling and standardised methods for supporting environmental sustainability with a special focus on Small and Medium Enterprises.

This international Networking, coordinated by ENEA (Italy), includes over 75 big institutions from 27 COST Countries (EU-zone: *Belgium, Bulgaria, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Israel, Italy, Latvia, The Former Yugoslav Republic of Macedonia, Netherlands, Norway, Poland, Portugal, Romania, Serbia, Slovenia, Spain, Sweden, Switzerland, Turkey, United Kingdom*) and 5 Non-COST Countries (extra-Europe: *Australia, Canada, China, Russia, USA*) to create a S&T critical mass in the environmental issues.

About the First International Workshop of COST Action TD1105 at Barcelona, 20 June 2013

The **Action Workshop** - *1st International Workshop of COST Action TD1105 on New Sensing Technologies and Transducers for Air Quality Monitoring* - will be organized one-day before 3rd MC Committee at Barcelona, as **Open Satellite Event** linked to *Transducers 2013*, chaired by the General Chair as Prof. Juan Ramon Morante (IREC), that is Action MC Member.

This **Workshop** will benefit from the presence of many involved Action MC members invited to participate at 3rd MC Committee at Barcelona on 21 June 2013, after closing of the international conference *Transducers 2013* (16 - 20 June 2013), edition jointly organized with *EuroSensors 2013* (European Conference on Sensors held annually in Europe). Very good visibility for the COST Action TD1105 *EuNetAir* should be provided by the *Transducers 2013* Conference Committee such as the logo of COST and/or Action TD1105 in the conference webpages, Action Satellite Workshop programme, and other expenditures for dissemination of achieved Action results.

The **Open Satellite Workshop** is composed by two Oral Sessions and one Poster Session. The accepted contributions (Oral/Poster) will be collected in a **Booklet** to be electronically distributed to the participants. In addition, a **Training School** (13-15 June 2013) of the COST Action TD1105 will be organized by Universitat de Barcelona (UB) and CSIC-IDAEA, Barcelona towards at least 20 reimbursed trainees and at least 4 reimbursed trainers, mainly from COST partnership. The Training School will be devoted to specific core-issues of COST Action TD1105 such as nanostructures, sensor materials, sensing technologies, environmental modeling of air-pollution, models, standards and protocols. Graduated students, PhD students, Post-Doc, Early Stage Researchers will be involved from COST partnership and COST Countries signing Memorandum of Understanding (MoU) in open way.

More Information

- Michele Penza, MC Chair/Proposer of *COST Action TD1105 EuNetAir*
ENEA - PO BOX 51 Br-4, I-72100 Brindisi – ITALY - michele.penza@enea.it
- Juan Ramon Morante, Action WG1 Leader and General Chair of *Transducers 2013 - EuroSensors XXVII*
IREC and UNIVERSITAT DE BARCELONA (UB), c/ Marti I Franques, 1 - E-08028 Barcelona - SPAIN - jrmorante@irec.cat



Thursday, 20 June 2013

COST Action TD1105 EuNetAir WORKSHOP

**Barcelona International Convention Centre (CCIB)
Plaça de Willy Brandt, 11-14, E- 08019 Barcelona, Spain**

16:00 - 20:00 COST Event Registration

16:30 - 18:30 **Session 1 - Sensors, Transducers and Signal Processing for Air-Quality Monitoring**
Chairperson: Eduard Llobet, Universitat Rovira I Virgili (URV), Tarragona, Spain

16:30 - 16:50 **COST Action TD1105: European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability. Overview and Plans of COST Action TD1105**
Michele Penza, Action Chair, ENEA, Brindisi, Italy

16:50 - 17:10 **Performance Analysis of Low-cost Gas Sensors for Air Quality Control: Overview in Europe and New Trends**
Michel Gerboles, JRC, EC DG ENV, Institute for Environment and Sustainability, Ispra, Italy

17:10 - 17:30 **Printed Environmental Sensors on Polymeric Foil: Status and Perspectives for Air-Quality Monitoring**
Danick Briand, EPFL, Institute of Microengineering, Neuchâtel, Switzerland

17:30 - 17:50 **Gas Sensor-Systems based on Hybrid Materials Dedicated to Air-Pollutants Monitoring**
Jerome Brunet, Université Blaise Pascal, LASMEA-CNRS, Aubiere, France

17:50 - 18:10 **Development of a Low-cost Mobile Sensor-System for Participatory Measurements of Urban Air Quality**
Jan Theunis, VITO, Mol, Belgium

18:10 - 18:30 **Computational Approaches to Wireless Chemical Sensing Challenges**
Saverio De Vito, ENEA, Portici (Naples), Italy

18:30 - 19:00 Break

18:30 - 19:00 **Poster Session**
Chairperson: Eduard Llobet, Universitat Rovira I Virgili (URV), Tarragona, Spain

19:00 - 20:00 **Session 2 - Materials for Chemical Sensors and Transducers**
Chairperson: Michele Penza, Action Chair - ENEA, Brindisi, Italy

19:00 - 19:20 **Carbon-based Nanomaterials for Gas Sensors of Environmental Interest**
Phil Martin, Non-COST Partner, CSIRO, Materials Science and Engineering, Lindfield, Australia

19:20 - 19:40 **Emerging Hybrid Materials for Air-Pollution Microsensors**
Marcel Bouvet, Action Sub-WG1.3 Leader, Université de Bourgogne, Dijon, France

19:40 - 20:00 **Conducting Polymer Sensor Arrays for Air-Quality Monitoring Applications**
Krishna Persaud, The University of Manchester, School of Chemical Engineering and Analytical Science, Manchester, United Kingdom

20:00 - 20:10 **Workshop Adjourns and Farewell**

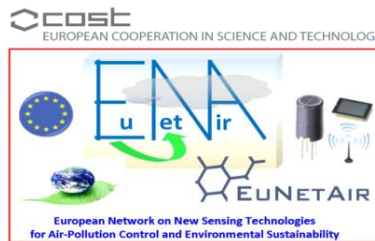
20:10 Closure of COST Action TD1105 EuNetAir Satellite WORKSHOP



FIRST INTERNATIONAL WORKSHOP on New Sensing Technologies and Transducers for Air-Quality Monitoring

Barcelona, 20 June 2013

Barcelona International Convention Centre (CCIB)
Plaça de Willy Brandt, 11-14, E- 08019 Barcelona, Spain



Action First Workshop Programme Committee

Michele Penza, ENEA, Brindisi, Italy
Juan Ramon Morante, IREC and Universitat de Barcelona, Spain
Albert Romano-Rodriguez, Universitat de Barcelona (UB), Spain
Juan Daniel Prades, Universitat de Barcelona (UB), Spain
Francisco Hernandez-Ramirez, IREC, Barcelona, Spain
Eduard Llobet, Universitat Roviri I Virgili, Tarragona, Spain
Annamaria Demarinis Loiotile, University of Bari, Italy

URL: www.cost.eunetair.it

URL: <http://transducers-eurosensors2013.org/>

COST Action TD1105 EuNetAir Steering Committee

Michele Penza, ENEA, Brindisi, Italy - *Action Chair*
Anita Lloyd Spetz, Linköping University, Sweden - *Action Vice-Chair*
Juan Ramon Morante, IREC, Spain
Andreas Schuetze, Saarland University, Germany
Ole Hertel, Aarhus University, Denmark
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Jan Theunis, VITO, Belgium
Marco Alvisi, ENEA, Brindisi, Italy
Gianluigi De Gennaro, University of Bari, Italy - *Grant Holder*
Fabio Galatioto, Newcastle University, UK
Ralf Moos, University of Bayreuth, Germany
Mar Viana, CSIC-IDAEA, Barcelona, Spain
Iveta Steinberga, University of Latvia, Riga, Latvia
Roberto Simmarano, Sensichips, Aprilia (Rome), Italy
Julian Gardner, University of Warwick, UK
Rod Jones, University of Cambridge, UK
Giorgio Sberveglieri, University of Brescia, Italy
Eduard Llobet, Universitat Roviri I Virgili, Tarragona, Spain
Thomas Kuhlbusch, IUTA eV, Duisburg, Germany
Albert Romano-Rodriguez, Universitat de Barcelona (UB), Spain
Annamaria Demarinis Loiotile, University of Bari, Italy - *Secretary*

WELCOME ADDRESS

This is a great honor and my pleasure to chair and welcome to ALL PARTICIPANTS of the **1st International Workshop** of our COST Action TD1105 *European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability - EuNetAir*.

This Workshop – held on 20 June 2013 - on ***New Sensing Technologies and Transducers for Air-Quality Monitoring*** has been organized as **Open Satellite Workshop** inside **Transducers 2013 - Eurosensors XXVII** - *The 17th International Conference on Solid-State Sensors, Actuators and Microsystems*, June 16-20, 2013, Barcelona, Spain.

This Workshop includes 9 Invited Speakers from at least 8 COST Countries and 6 Poster Presentations with the co-authors from at least 10 COST Countries.

The concerted COST Action TD1105 *EuNetAir* - related to R&D issues of the air quality monitoring including environmental technologies, nanomaterials, gas sensors, smart systems, air-pollution modelling, measurements, methods, standards and protocols - is very pleased to connect international specialists and excellent scientists to create a networking of Pan-European R&D platform from 27 COST Countries and 5 Non-COST Countries. Most part of COST Countries are represented in this Meeting.

On behalf of Action Management Committee, I would like to thank ALL Workshop participants, Local Organizing Committee and General Chair of *Transducers 2013* (Prof. Juan Ramon Morante) to give us this opportunity to disseminate the results of the COST Action TD1105 *EuNetAir* towards a wide international targeted audience, that with their valuable scientific work, kind availability and great enthusiasm will make our Action Workshop very successful !

Barcelona, 14 June 2013

Michele Penza, ENEA, Italy
COST Action TD1105 Chair
michele.penza@enea.it

LIST OF PRESENTERS

Invited Talks

COST Action TD1105: European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability. Overview and Plans of COST Action TD1105

Michele Penza, Action Chair, ENEA, Brindisi, Italy

Performance Analysis of Low-cost Gas Sensors for Air Quality Control: Overview in Europe and New Trends

Michel Gerboles, JRC, EC DG ENV, Institute for Environment and Sustainability, Ispra, Italy

Printed Environmental Sensors on Polymeric Foil: Status and Perspectives for Air-Quality Monitoring

Danick Briand, EPFL, Institute of Microengineering, Neuchâtel, Switzerland

Gas Sensor-Systems based on Hybrid Materials Dedicated to Air-Pollutants Monitoring

Jerome Brunet, Université Blaise Pascal, LASMEA-CNRS, Aubiere, France

Development of a Low-cost Mobile Sensor-System for Participatory Measurements of Urban Air Quality

Jan Theunis, VITO, Mol, Belgium

Computational Approaches to Wireless Chemical Sensing Challenges

Saverio De Vito, ENEA, Portici (Naples), Italy

Carbon-based Nanomaterials for Gas Sensors of Environmental Interest

Phil Martin, Non-COST Partner, CSIRO, Materials Science and Engineering, Lindfield, Australia

Emerging Hybrid Materials for Air-Pollution Microsensors

Marcel Bouvet, Action Sub-WG1.3 Leader, Université de Bourgogne, Dijon, France

Conducting Polymer Sensor Arrays for Air-Quality Monitoring Applications

Krishna Persaud, The University of Manchester, School of Chemical Engineering and Analytical Science, Manchester, United Kingdom

Poster Presentations

CO₂ GAS SENSOR BASED ON MIS STRUCTURE WITH LAF₃ LAYER

I.R.Shandova¹, A.V.Varfolomeev¹, A.A.Vasiliev^{1,2}, A.S.Lagutin¹, W.Moritz³

¹National research center Kurchatov Institute, Moscow, Russia

DETECTION OF LOW CONCENTRATIONS OF VOLATILE ORGANIC COMPOUNDS WITH SIC-FIELD EFFECT TRANSISTORS

C. Bur^{1,2}, A. Schütze¹, J. Eriksson², A. Lloyd Spetz², M. Andersson², and D. Puglisi²

¹Lab for Measurement Technology, Saarland University, D-66123 Saarbrücken, Germany

²Dept. of Physics, Chemistry and Biology, Div. of Applied Sensor Science, Linköping University, SE-58183 Linköping, Sweden

ENSEMBLE AVERAGING FOR LOW-POWER GAS DETECTION USING INDIVIDUAL CARBON NANOTUBES

K. CHIKKADI¹, S. NUFER¹, W. LIU¹, M. HALUSKA¹, CH. HIEROLD¹,

Micro and Nanosystems, ETH Zurich

OVERVIEW OF ENVIRONMENTAL MEASUREMENTS: ATMOSPHERIC POLLUTION

Viana M., Querol X., and the IDAEA-CSIC research team

¹Institute for Environmental Assessment and Water Research, Jordi Girona 18, 08034 Barcelona, Spain

AIR QUALITY MONITORING PORTABLE SENSOR SYSTEM

D. Suriano, R.Cassano, M.Alvisi and M.Penza

ENEA - Italian National Agency for New Technologies, Energy and Sustainable Economic Development,
Technical Unit for Materials Technologies-Brindisi Research Center, PO Box 51 Br-4, I-72100 Brindisi, Italy.

EMISSION MONITORING AND CONTROL BY GAS AND PARTICLE SENSORS FOR CLEAN ENVIRONMENT

A. Lloyd Spetz^{1,2}, C. Bur^{2,3}, J. Huotari¹, Z. Darmastuti², J. Lappalainen¹, H. Jantunen¹,
R. Bjorklund², P. Möller², A. Schütze³ and M. Andersson^{1,2}

¹*Microelectronics and Material Physics Laboratories, Universtiy of Oulu, Oulu, Finland*

²*Div. of Applied Sensor Science, Linköping University, Linköping, Sweden*

³*Lab for Measurement Technology, Saarland University, Saarbrücken, Germany*

COST ACTION TD1105 ON NEW SENSING TECHNOLOGIES FOR AIR-POLLUTION CONTROL AND ENVIRONMENTAL SUSTAINABILITY: OVERVIEW IN EUROPE AND PLANS

M. Penza

ENEA - Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Technical Unit for Materials Technologies-Brindisi Research Center, PO Box 51 Br-4, I-72100 Brindisi, Italy. Email: michele.penza@enea.it

Abstract

This is a short overview of the COST Action TD1105 *EuNetAir - European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability* - funded in the framework *European Cooperation in the field of Scientific and Technical Research* (COST) during the period 2012-2016.

The main objective of the Concerted Action is to develop new sensing technologies for Air Quality Control at integrated and multidisciplinary scale by coordinated research on nanomaterials, sensor-systems, air-quality modelling and standardised methods for supporting environmental sustainability with a special focus on Small and Medium Enterprises.

This international Networking, coordinated by ENEA (Italy), includes over 75 big institutions from 27 COST Countries (EU-zone: *Belgium, Bulgaria, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Israel, Italy, Latvia, The Former Yugoslav Republic of Macedonia, Netherlands, Norway, Poland, Portugal, Romania, Serbia, Slovenia, Spain, Sweden, Switzerland, Turkey, United Kingdom*) and 5 Non-COST Countries (extra-Europe: *Australia, Canada, China, Russia, USA*) to create a S&T critical mass in the environmental issues.

This COST Action [1, 2] (see logo in Fig. 1) will focus on a new detection paradigm based on sensing technologies at low cost for Air Quality Control (AQC) and set up an interdisciplinary top-level coordinated network to define innovative approaches in sensor nanomaterials, gas sensors, devices, wireless sensor-systems, distributed computing, methods, models, standards and protocols for environmental sustainability within the European Research Area (ERA).

The state-of-the-art showed that research on innovative sensing technologies for AQC based on advanced chemical sensors and sensor-systems at low-cost, including functional materials and nanotechnologies for eco-sustainability applications, the outdoor/indoor environment control, olfactometry, air-quality modelling, chemical weather forecasting, and related standardisation methods is performed already at the international level, but still needs serious efforts for coordination to boost new sensing paradigms for research and innovation. Only a close multidisciplinary cooperation will ensure cleaner air in Europe and reduced negative effects on human health for future generations in smart cities, efficient management of green buildings at low CO₂ emissions, and sustainable economic development.

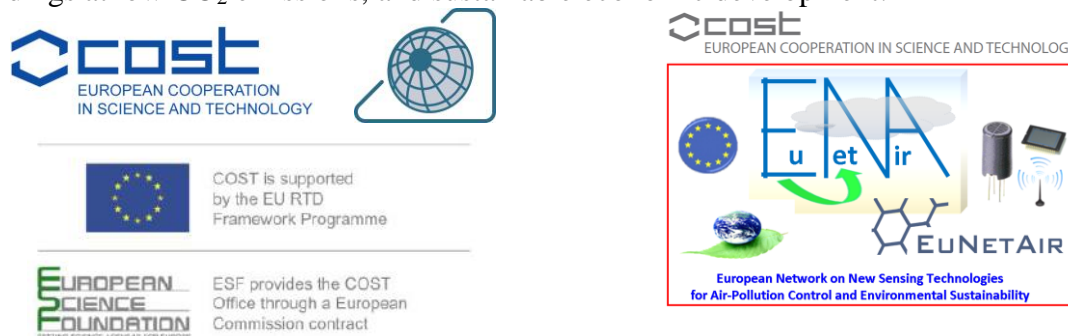


Figure 1. COST Office, ESSEM Domain and Action TD1105 EuNetAir Logo.

The aim of the Action is to create a cooperative network to explore new sensing technologies for low-cost air-pollution control through field studies and laboratory experiments to transfer the results into preventive real-time control practices and global sustainability for monitoring climate changes and outdoor/indoor energy efficiency. Establishment of such a European network, involving Non-COST key-experts, will enable EU to develop world capabilities in urban sensor technology based on cost-effective nanomaterials and contribute to form a critical mass of researchers suitable for cooperation in science and technology, including training and education, to coordinate outstanding R&D and promote innovation towards industry, and support policy-makers. Main objectives of Action are listed, but not limited to:

- to establish a top-level Pan-European multidisciplinary R&D platform on new sensing paradigm for AQC contributing to sustainable development, green-economy and social welfare
- to create collaborative research teams in the ERA on the new sensing technologies for AQC in an integrated approach to avoid fragmentation of the research efforts
- to train Early Stage Researchers (ESR) and new young scientists in the field for supporting competitiveness of European industry by qualified human potential
- to promote gender balance and involvement of ESR in AQC
- to disseminate R&D results on AQC towards industry community and policy makers as well as general public and high schools.

The Workplan is organized in four complementary Working Groups (WGs), each devoted to a progressive development of synthesis, characterization, fabrication, integration, prototyping, proof-of-concepts, modeling, measurements, methods, standards, tests and application aspects. The four WGs with the specific objectives are:

- **WG1:** *Sensor materials and nanotechnology*
- **WG2:** *Sensors, devices and sensor-systems for AQC*
- **WG3:** *Environmental measurements and air-pollution modeling*
- **WG4:** *Protocols and standardisation methods*

This Action will focus on the study of sensor nanomaterials and nanotechnologies exhibiting unique properties in terms of chemical and thermal stability, high sensitivity, selectivity. Nanosize effects of functional materials will be explored for integration in the gas sensors at low power-consumption. Furthermore, specific nanostructures with tailored sensing properties will be developed for gas sensors and sensor-systems with advanced functionalities.

Selected high-quality research products and innovative technologies developed by the partnership of COST Action TD1105 are shown in the Figure 2.

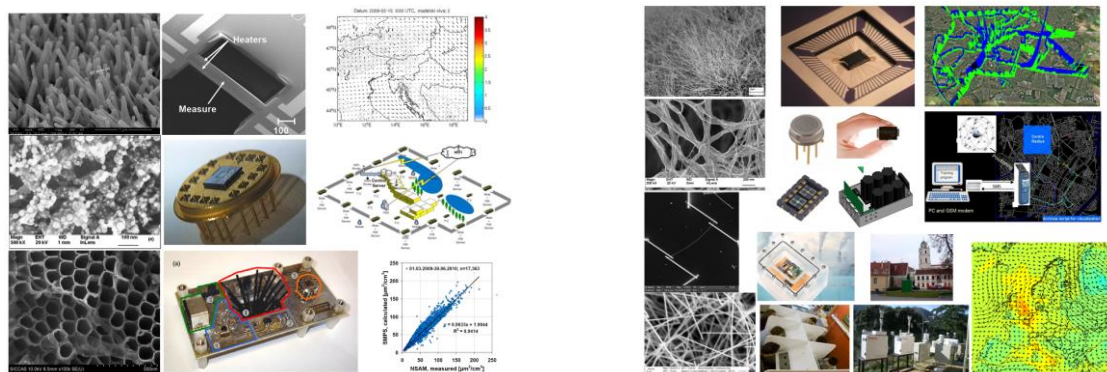


Figure 2. Selected R&D technological products developed by some partners (academia, research institutes, agencies, industry) involved in the COST Action TD1105 *EuNetAir*. Courtesy from *EuNetAir* partnership.

References

1. Action Memorandum of Understanding: http://www.cost.eu/domains_actions/essem/Actions/TD1105
2. Action website: <http://www.cost.eunetair.it>

PERFORMANCE ANALYSIS OF LOW-COST GAS SENSORS FOR AIR QUALITY CONTROL

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Abstract

Metrology for Chemical Pollutants in Air (MACPoll) is a joint research project of the European Metrology Research Programme of EURAMET that among other activities deals with low-cost gas sensors for air quality monitoring. Gas sensors are identified as emerging measuring devices for “indicative measurements” regulated in the Air Quality Directive [1]. Compared to reference measurements [2], gas sensors would allow air pollution monitoring at a lower cost. The Directive allows using indicative measurements without restriction in the zones where the upper assessment threshold (UAT) is not exceeded while they permit a reduction of 50 % of the minimum reference measurements where the UAT is exceeded. The Directive does not specify any indicative method but it requires to demonstrate that they can meet a data quality objective (DQO) that is about twice less stringent than the one of reference methods. The DQO is defined as a relative expanded uncertainty. Since the Directive does not give any guidance for this demonstration, within MACPoll it has been decided to draft such a protocol [3] using related literature [4].

The protocol requires to identify the sensor, manufacturer and supplier, model, p/n, test board, power supply, data acquisition, treatment and processing and other relevant information like the heater and cycle temperature, the protection box and/or sensor holder. The evaluation of the sensor is carried out against a limit or target value (LV) defined in the Directive with a corresponding averaging time. The selection of the micro-environment (urban, rural or suburban areas for background, traffic or industrial monitoring sites) in which it is planned to use the sensor allows estimating the full scale of the sensor, the abundance of possible gaseous interferences, the average temperature and relative humidity of exposure. Existing information about the sensitivity, selectivity (known interference), stability and existing validation data shall be gathered including, if available, a model equation describing sensor responses according to influencing parameters.

The objective of this evaluation protocol may be different according to the knowledge of the model equation used for the sensors. One may distinguish:

- sensors behaving as a black box: the test results of this protocol can be used to directly estimate the measurement uncertainty induced by the variation of influencing parameters or after setting up a correction function to compensate for these effects.
- sensors displaying measurements, but for which a model equation describing how sensor values are computed is also available: the results of the tests can be used to estimate the measurement uncertainty induced by influencing parameters with or without adjustment of the coefficients of the model equation that compensates for these effects.
- sensors for which only a model equation is given with which users shall compute sensor responses: the results of the tests are used to estimate uncertainty after adjusting the coefficients of the model equation.
- nothing is known about the relationship between sensor responses and the concentrations of the tested gas pollutant. In this case, the results of the tests are used to set up a model equation and to estimate the resulting measurement uncertainty.

A dynamic system for generating, known concentrations of a test gas is necessary. An exposure chamber of inert materials shall be used for the simultaneous test of several sensors. It must be possible to measure, control and change the rate of airflow through the chamber and the concentration of the test gas, temperature, relative humidity and any added gaseous interference.

All parameters shall be controlled independently to avoid the effect of uncontrolled variables on sensor responses are attributed to controlled parameters. The evaluation of sensors shall only rely on the comparison between sensor responses and reference measurements excluding data calculated from the gas mixture generation system.

The response time of sensors is evaluated as 90% of the final stable value, when concentration changes from 0 to 80 % of the full scale. It is used to set the length of all tests of the protocol and to check if the sensor is able to reach stability within averaging time.

Then, a pre-calibration of the sensor is performed at several concentration levels over the full scale, at the average exposure conditions. The objective of this calibration is to eliminate any bias at the mean temperature and relative humidity and to establish a draft model equation if needed.

Then repeatability, short and long term drifts of the sensor are determined by calculating the standard deviation of sensor values for 3 consecutive averaging time periods, three consecutive days and every 2 weeks during three months of use, respectively. Hysteresis is evaluated by repeating the pre-calibration experiment in an increasing ramp, a decreasing ramp and an increasing ramp of test gas, consecutively. Repeatability figures impose limits on the accuracy of the calibration. The short term stability is used to set the maximum time between similar tests. If a trend in the long term drift or significant hysteresis or interference (see below) effects are identified, they might be included into the model equation or treated as sources of uncertainty.

The next step is the identification of significant interferences. The tests are all performed one at time at the mean concentration of the test gas with all influencing variables kept constant. Temperature and humidity are tested between mean-10 °C and mean+10 °C by step of 5 °C and between mean-20% to mean+20% by step of 10% respectively. The sensor response is also tested using filtered air, laboratory air and ambient air. Gaseous interferences are tested at two levels: at zero level and at the expected average values observed in the selected micro-environment [5]. For some sensors, ambient pressure, power supply and wind velocity shall be tested.

Finally a design of experiments for validation/modeling is set up: the test levels of the pre-calibration experiment are tested at 3 temperatures (mean-10 °C, mean and mean+10 °C) under 3 relative humidity (mean-20 %, mean and mean+20%) and at 2 levels of any parameter found to be significant (0 level and its average value for the selected micro-environment). The laboratory measurement uncertainty is estimated with these test results either by evaluating the differences between the black-box sensor values and the reference measurements [4] or by application of the law of propagation of error [6] if a model equation exists. A gas sensor is rejected when the laboratory uncertainty exceeds the DQO.

An appropriate test site of the intended field of application of the sensor is selected regarding its exposure conditions. A test of at least three months should be employed which shall include periods representative of the extremes likely to be encountered in the selected micro-environment of the sensor. The monitoring sites should be equipped with reference methods of measurements for the gaseous pollutants of interest and influencing variables. The field uncertainty is calculated by comparing the sensor results with the reference measurements using the methodology described in [4]. A gas sensor is accepted as indicative method if the field uncertainty does not exceed the DQO.

References

1. Directive 2008/50/EC of the European Parliament and the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, Official Journal of the European Union L 152/1 of 11.6.2008
2. Guide for Local Authorities, Purchasing Air Quality Monitoring Equipment, AEAT/ENV/R/2088 Issue 2, August 2006, UK
3. MACPoll, WP4, Revision of the validation protocol and procedure for calibration, D4.3.3, vs 1, Jun 2013
4. Guide to the demonstration of equivalence of ambient air monitoring methods, Report by an EC Working Group on Guidance
5. MACPoll, WP4, Selection of suitable micro-sensors for validation, D4.3.1 , vs 1, Mar 2012
6. JCGM, 2008. Evaluation of measurement data — Guide to the expression of uncertainty in measurement

PRINTED ENVIRONMENTAL SENSORS ON POLYMERIC FOIL: STATUS AND PERSPECTIVES FOR AIR-QUALITY MONITORING

D. Briand¹

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Abstract

During the last decade, we have seen the emergence of sensing technologies integrated on polymeric and flexible substrates. Besides the new functionalities enabled by the use of such substrates, there is also a strong potential for their cost-effective manufacturing using large area fabrication techniques, such as printing. These devices could be integrated in wireless smart sensing labels and be a key technology for the future deployment of the internet of things.

There have been several research publications on the development and integration of polymeric and foil based environmental sensors [1]. We will review the recent developments in the field including our own work on flexible gas sensors for wireless applications. We will discuss the advantages and drawback of the realisation of gas sensors on polymeric foil in relation with the different transducers already demonstrated: capacitive, resistive, colorimetric, FET... Sensitivity, power consumption and robustness are important characteristics for their application in air quality monitoring. Performing temperature and humidity sensors have been reported and integrated in smart sensing RFID labels. However, progresses are required on printed and foil based gas sensors to reach the requirements for their application in cost-effective distributed air quality monitoring systems. We will highlight these challenges and propose research topics that need to be addressed to make a step forward.

Looking at sensors, we have shown, in partnership with the University of Tübingen, ultra-low power capacitive sensors on polymeric foil for humidity and VOCs detection. Resistive, conducting polymer and semiconductors (metal-oxide, CNT, etc) gas sensors are of high interest. However, their implementation on foil has to face the worse pattern resolution achieved when using printing and the limitation in processing temperature due to the polymeric nature of the substrate. We will present our progresses made towards fully printed micro-hotplates on PEN and PI foil for both conductor polymer and metal-oxide gas sensors. Sensitivity needs to be improved and power consumption to be decreased for their direct integration into air quality monitoring labels. We are therefore investigating the use of nanostructured sensing materials and methods for their incorporation onto polymeric transducers. We will especially address the challenges towards the fully printing of these sensors and their integration into foil based smart sensing systems.

Finally, we will conclude by proposing smart sensing systems on foil for distributed air quality monitoring. With the co-integration of printed devices and functionalities with silicon components, cost-effective sensing modules on polymeric foil could be distributed in the indoor and outdoor environments. They could communicate via wireless communication or could be wirelessly addressed or remotely powered by the users, being implemented on walls, objects, people, or directly into mobile phones.

References

[1] D. Briand, A. Oprea, J. Courbat, N. Barsan, Making environmental sensors on plastic foil, *Materials Today*, 14(9) (2011) 416-423.

GAS SENSOR-SYSTEMS BASED ON HYBRID MATERIALS DEDICATED TO AIR-POLLUTANTS MONITORING

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Objective and motivations

The monitoring of atmospheric pollutants by gas sensors requires devices with high-level metrological characteristics. The sensitivity, the repeatability, the threshold of detection and the selectivity must be especially optimized. Therefore, our recent works have been focused on efficient gas sensor systems for the metrology of oxidizing species (nitrogen dioxide: NO₂, ozone: O₃) and aromatic hydrocarbons (BTX) in low atmosphere. These objectives are motivated by both the hazardous properties of the target gases [1,2] and the necessity to ensure their monitoring to ensure safe living and working conditions [3,4].

This lecture is focused on the developments of original organic/inorganic hybrid materials and their implementation in gas sensor systems. Their reactivity with gases makes them appropriate either as chemical filters to improve the selectivity of existing sensors or for the achievement of new sensing devices. These two perspectives have been investigated.

Sensor system for oxidizing pollutants monitoring

The relevance of phthalocyanine-based chemoresistors for the measurement of O₃ in urban atmosphere has been previously reported [5]. Moreover, the successful selective monitoring of NO₂ by indigo/phthalocyanine bilayer sensing structure, indigo nanolayer acting as selective ozone filter was detailed in reference [6]. Nevertheless, the lifetime of the filtering layer remains restricted by both the low specific surface area of indigo and the ozonolysis reaction mainly localized at the surface. In order to enhance the filtering durability by increasing the surface/volume ratio of indigo, a hybrid material was developed. It was obtained by the functionalization of carbon nanotubes exhibiting a high specific surface area by indigo particles still acting as active sites for O₃ removal.

This indigo/nanocarbon hybrid material has been characterized by SEM, XRD, TGA analysis and a non-covalent functionalization has been established. Gas exposures reveal its filtering selectivity towards O₃ (no NO₂ removal) and its higher durability as compared to carbon nanotubes and indigo separately (Fig.1). The sensitivity, the repeatability and the lifetime enhancement towards NO₂ of phthalocyanine-based chemoresistor by the implementation of such hybrid material will be illustrated (Fig.2) and argued.

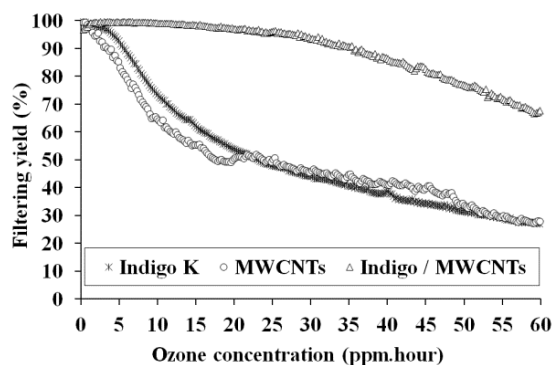


Figure 1. Filtering yield of indigo, carbon nanotubes and hybrid material towards ozone.

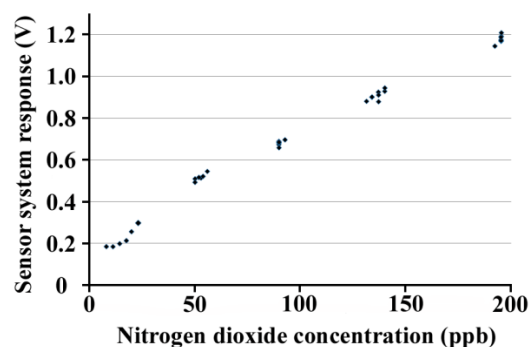


Figure 2. Calibration curve of sensor microsystem towards nitrogen dioxide.

Sensing structures for BTX detection

Despite of many reports devoted to Benzene, Toluene and Xylenes (BTX) measurement [7-9], their accurate detection remains a real challenge. Because of their highly delocalized π system, metallophthalocyanines (MPcs) are relevant materials to interact both with aromatic analytes as BTX and with substrates having a high strong aromatic nature like carbonaceous material. Therefore, sensing structures implementing functionalized carbon nanotubes by phthalocyanine active groups as sensitive material have been developed. Taking into consideration the interactions involved between target gases and the sensitive layer, QCM was chosen as transducing mode. Since Nanocarbonaceous materials exhibit high specific surface areas, a great sensitivity is expected.

The hybrid material has been characterized by TEM (Fig. 3), UV-vis spectroscopy and TGA. All results corroborate the non-covalent functionalization of carbon nanotubes by phthalocyanine. Measurements on QCM sensors emphasize the best sensitivity obtained towards toluene for devices made with hybrid material as compared to phthalocyanine and carbon nanotubes separately (Fig. 4). The influence of specific surface area of the sensitive material on sensor response is so manifest. The low working temperature (room temperature) must be also pointed out.

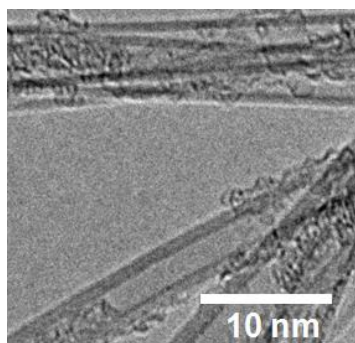


Figure 3. TEM micrograph of ttb-CuPc / CNTs hybrid material.

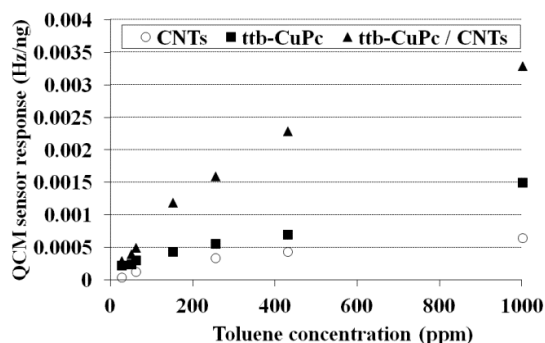


Figure 4. QCM sensor responses towards toluene.

References

1. International Center for Technology Assessment, "In-Car Air Pollution: The Hidden Threat to Automobile Drivers: Report No. 4", An Assessment of the Air Quality Inside Automobile Passenger Compartments, July 2000.
2. R. Snyder, C. Hedli, "An overview of benzene metabolism", *Environ Health Perspectives* **6** (1996) 1165.
3. J.H.V. Wijnen, A.P. Verhoeff, H.W.A. Jans, M.V. Bruggen, The exposure of cyclists, car drivers and pedestrians to traffic-related air pollutants, *Int. Arch. Occup. Environ. Health* **67** (1995) 187-193.
4. Su F., C. Lu, S. Hu, "Adsorption of benzene, toluene, ethylbenzene and p-xylene by NaOCl-oxidized carbon nanotubes", *Colloids and Surfaces Journal A: Physicochemical and Engineering Aspects*, **353** (2010) 83-91.
5. J. Brunet, A. Pauly, L. Mazet, J.P. Germain, M. Bouvet, B. Malezieux, "Improvement in real time detection and selectivity of phthalocyanine gas sensors dedicated to oxidizing pollutants evaluation", *Thin Solid Film* **490** (2005) 28-35.
6. J. Brunet, L. Spinelle, A. Pauly, M. Dubois, K. Guerin, M. Bouvet, C. Varenne, B. Lauron, A. Hamwi, "All-organic device with integrated chemical filter dedicated to the selective measurement of NO₂ in air", *Organic Electronics* **11** (2010) 1223-1229.
7. Y. Ueno, T. Horiuchi, O. Niwa, H.-S. Zhou, T. Yamada, I. Honma, "Portable Automatic BTX Measurement System with Microfluidic Device using Mesoporous Silicate Adsorbent with Nano-sized Pores", *Sensors and Actuators B: Chemical* **95** (2003) 282-286.
8. B. Yulianto, Y. Kumai, S. Inagaki, H. Zhou, "Enhanced benzene selectivity of mesoporous silica SPV sensors by incorporating phenylene groups in the silica framework", *Sensors and Actuators B: Chemical* **138** (2009) 417-421.
9. Y. Gurbuz, W.P. Kang, J. L. Davidson, D.V. Kerns, "Diamond microelectronic gas sensor for detection of benzene and toluene", *Sensors and Actuators B: Chemical* **99** (2004) 207-215.

DEVELOPMENT OF A LOW-COST MOBILE SENSOR-SYSTEM FOR PARTICIPATORY MEASUREMENTS OF URBAN AIR QUALITY

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Introduction

Exposure of people to health-relevant air pollutants is poorly described by concentrations measured in official monitoring stations [1]. Novel strategies to increase the spatial coverage of air quality measurements include mobile and participatory monitoring. The EveryAware project investigates the use of off-the-shelf available low-cost sensors to estimate people's exposure to traffic-related pollution. A portable sensor box with an array of electrochemical and metal oxide gas sensors was developed [2]. Machine learning techniques were used for multivariate field calibration. Black Carbon (BC), a good indicator for exposure to traffic-related pollution and associated health impacts [3], was chosen as a target for the estimates.

Material and Methods

25 sensor boxes were collocated with 3 micro-aethalometers (microAeth® Model AE51) on a traffic location in Turin in January 2013. This resulted in about 5 days of stationary data deemed valid for calibration purposes at a 1 second resolution. Approximately 3 hours of mobile measurements were recorded by one sensor box and one micro-aethalometer. More extensive mobile data are currently collected. Measurements from the first two days after start-up were excluded based on strong drifting of various sensors. No further sensor data cleaning was performed. Known effects such as cross-interference, drift or temperature and humidity effects are thus prevalent in the data. A noise reduction algorithm ([7]) was applied to decrease the noise on the target BC measurements. A 5 minute moving average filter was applied to both sensor and BC data to level their differing auto-correlation.

Machine learning techniques (Artificial Neural Networks (ANN), random forests (RF) and Support Vector Machines (SVM)) were assessed for establishing a model to estimate BC concentration based on sensor box measurements. The ANN was a feedforward neural network with 1 hidden layer of 10 neurons. For all three machine learning techniques, the regression problem has been approached in the same way. One data point consisted of ten features, i.e. one value for each sensor plus temperature and humidity. The target was the BC value of the micro-aethalometers. Hyper-parameters of the different models were optimized in empirical analyses. Two comparative analyses were made: (i) training and testing of models on temporally independent data (one round cross-validation), and (ii) interchangeability of models between sensor boxes.

Results

The models have proven well fitted to simulate the general patterns in the data. The evaluation statistics for longer time series in the temporally independent model testing differed considerably between the models. ANN and SVM had significantly better performance in comparison to RF, which overfitted the data and had a higher generalization error. We found also that local fluctuations were difficult to retrieve. We believe this is due to the lower sensitivity of the sensors compared to the micro-aethalometer. This explains the relative low performance for the shorter time scales of the mobile measurements (e.g. ANN: $R^2 = 0.38$, $rmse = 1.7 \mu\text{g}/\text{m}^3$; RF: $R^2 = 0.11$, $rmse = 2.3 \mu\text{g}/\text{m}^3$; SVM: $R^2 = 0.17$, $rmse = 1.9$

$\mu\text{g}/\text{m}^3$). Based on the model comparison, the ANN was selected for the final implementation. The interchangeability of models between sensor boxes was observed to be high, with values for the evaluation statistics that are similar to the results of the temporally independent testing (Figure 1). Cumulative values are also displayed. This shows how general patterns are captured by the model, resulting in comparable cumulative functions.

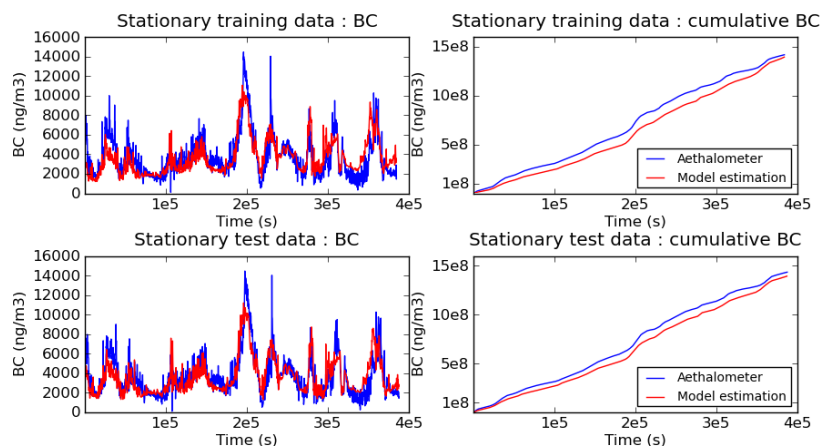


Figure 1. Interchangeability of the calibration model on stationary data (the top panel shows the model fit, the bottom panel the BC estimations for another SB using the same model).

In Figure 2, the same curves are shown for mobile test data. While general trends are still preserved, some local peak events are missed by the model. Although the current model is only suitable for exposure to BC assessment over longer integration periods rather than for peak assessment, the model is currently implemented in the AirProbe Beta mobile app. The app mediates the communication between the sensor boxes and the EveryAware servers. This is already used for a local test case in Turin, Italy. Meanwhile, research on further improvement of the calibration model is conducted.

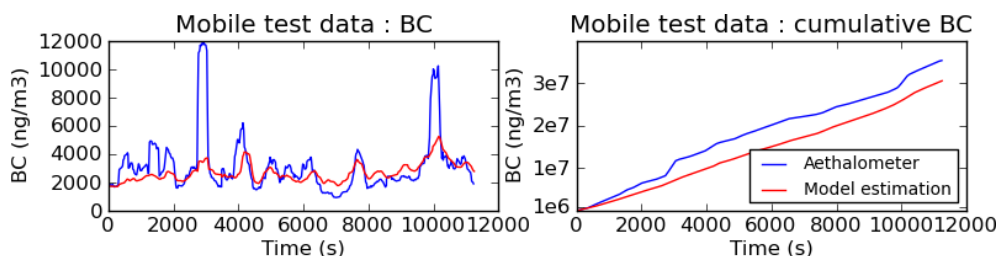


Figure 2. Estimated BC for mobile test data.

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References

1. S. Kaur, M. Nieuwenhuijsen, R. Colvile, "Fine particulate matter and carbon monoxide exposure concentrations in urban street transport microenvironments" *Atmosph. Environment* **41** (2007) 4781–4810.
2. B. Elen, J. Theunis, S. Ingarra, et al, "The EveryAware SensorBox: a tool for community-based air quality monitoring", *Sensing a Changing World*, Wageningen (Netherlands), May 2012.
3. N. Janssen, et al, "Black Carbon as an Additional Indicator of the Adverse Health Effects of Airborne Particles Compared to PM10 and PM2.5" *Environmental Health Perspectives* **119** (2011) 1691-1699.
4. G. Hagler, T. Yelverton, et al, "Post-processing Method to Reduce Noise while Preserving High Time Resolution in Aethalometer Real-time Black Carbon Data" *Aerosol and Air Quality Research*, **11**(2011), 539–546.

COMPUTATIONAL INTELLIGENCE APPROACHES TO DISTRIBUTED CHEMICAL SENSING CHALLENGES

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Abstract

The estimation of chemicals distribution is generally recognized as significantly relevant for citizens safety and for the definition of integrated urban and mobility plans designed to face air pollution in cities. Actually, chemicals monitoring can be of paramount importance for several applications ranging from olfactive nuisance monitoring to security e.g. for the detection of explosives and drug factories in cities. However, chemicals monitoring both in outdoor and indoor environment is affected by the peculiarity of chemicals propagation process: diffusion and turbulence make a single point of measure ineffective, calling for distributed approaches to chemicals detection and concentration estimation. Costs and deployment considerations require the monitoring task to be fulfilled by a network of wireless (sometime mobile) modules, with the wireless term being related to either connectivity and/or power supply (Wireless Chemical Sensor Networks, WCSN). A number of challenges repeatedly recurs when engineer try to design real world operating WCSN systems. In facts, single module calibration and sensor stability, efficient power usage and cooperative reconstruction seems to be the most common challenges to face both in indoor and outdoor settings. In this contribution, our point is to show the possibilities offered by a computational intelligence approach to these issues together with some interesting results obtained by our and several groups involved in the challenges. In facts, integrating continuous advances in sensor devices technology, computational intelligence techniques, by processing sensors data and eventually embedded on sensor nodes, offers viable, low cost solution to some of the trickiest problems we face, exploiting sensor arrays partial selectivity, counteracting drift and reconstructing a 3D gas image of the sensed environment. One of the example we show relates with the calibration of solid state multisensory devices for air pollution monitoring. A controlled atmosphere, in-lab, model based approach have shown several limitations (see for example [1]) due to the dimensionality of the complex gas mixtures and complexities of models taking into account selectivity issues. Starting from 2007, we proposed an on-field calibration strategy, that, based on a statistical regressors approach, allowed us to reach interesting performances. The approach relied on the use of a spectrometers based station as a reference for the on-field calibration of a small multisensor device. In our testbed, a feed forward neural network trained using a 10 days measurements set, was capable to gain a relative estimation error for benzene of about 0.01 (1%) during more than 6 months. However the onset of sensor and concept drift effects required a recalibration procedure to be performed every 6 months (see Fig.1). In truth, for this approach to be considered feasible in terms of deployment of hundreds of modules, the possibility to use only a small number of samples as a training set become crucial. An interesting solution could be based on the implementation of on-line learning strategies i.e. having a mobile spectrometer based station provide ground truth values on a regular (or uneven) basis adapting the non-linear calibration of the modules. At the best of our knowledge, this approach has never been implemented, as an extension of this idea, we proposed the use of Semi-Supervised learning process adapting the learnt module calibration exploiting the significant availability of unlabeled samples (see Fig. 2) [2]. In a very similar framework, Tsujita et al. proposed an interesting automatic on-field recalibration transfer scheme that could be useful for facing the sensor stability issues [3]. In that paper an easy way to cooperatively share and use the information on base sensor response for continuous calibration was proposed and tested.

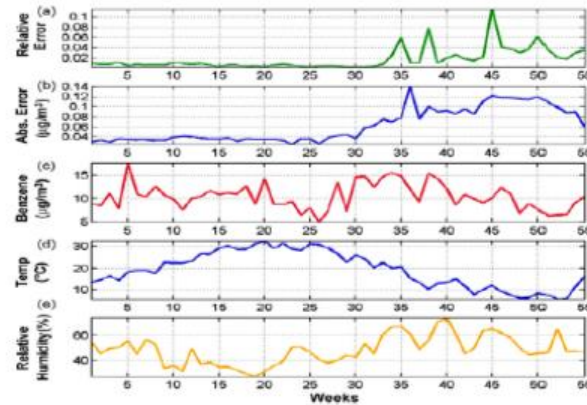


Fig. 1. On Field calibration of a GPRS-enabled MOX based multisensory device for pollution monitoring. Measured error is comparable with the datasheet properties of conventional analyzer for about 6-months after that sensors and concept drift onset severely affected obtained calibration. COST Action TD1105 *EuNetAir* 1st International Workshop, Open Satellite Workshop inside *Transducers 2013*, Barcelona, 20 June 2013.

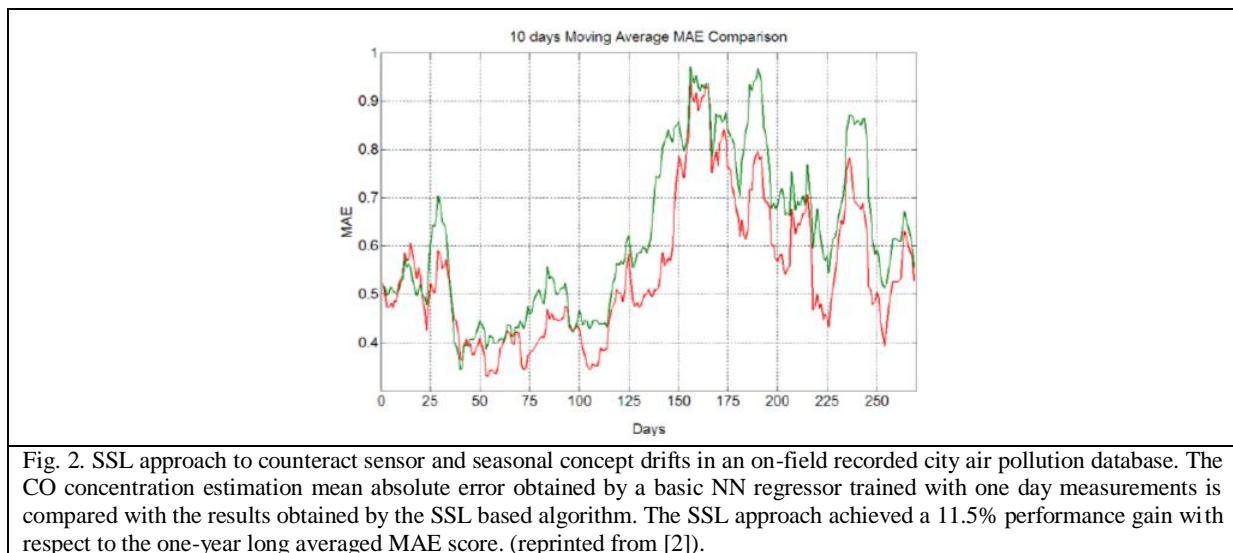


Fig. 2. SSL approach to counteract sensor and seasonal concept drifts in an on-field recorded city air pollution database. The CO concentration estimation mean absolute error obtained by a basic NN regressor trained with one day measurements is compared with the results obtained by the SSL based algorithm. The SSL approach achieved a 11.5% performance gain with respect to the one-year long averaged MAE score. (reprinted from [2]).

In the last decade, several research papers investigated the possibility to monitor the indoor air quality for multiple applications scenario ranging from safety to security and energy efficiency. Due to the complexities of chemical signal propagation in indoor environments, the use of a distributed network of analyzers is mandatory but sensor power needs limits survivability in terms of energy supply when dealing battery operated nodes. Recently low power sensor technologies and operating strategies seems promising (see [4]), however the needs arise to address data transmission power needs. Sensor censoring, that is the capability to discharge non relevant acquisition, is a possible solution to the cost of non relevant data transmission. Simple threshold based approaches may fail or be difficult to tune in the chemical sensor scenario due to the complex response of the sensors array itself. We proposed to embed a local computational intelligence software component actually implementing an on board neural network to make the module capable to locally estimate the concentration of two mock pollutants for which its sensor array was calibrated [5]. In such a way, the node can be capable to estimate the concentration of a relevant pollutant neglecting the presence of interferences reducing the need for uninformative data transmissions. The capability to reconstruct the concentration of chemicals in a 3D environment is usually the final stage in an integrated indoor or outdoor chemical monitoring system, in [6], we have shown this capability for the same platform when in a networked deployment by relying in an adaptation of the algorithm proposed in [7].

In conclusion, the work of our group and several researchers has definitely shown that computational intelligence techniques can represent an interesting reservoir for the counteraction of several issues that limit the achieving of a truly distributed air quality monitoring capability.

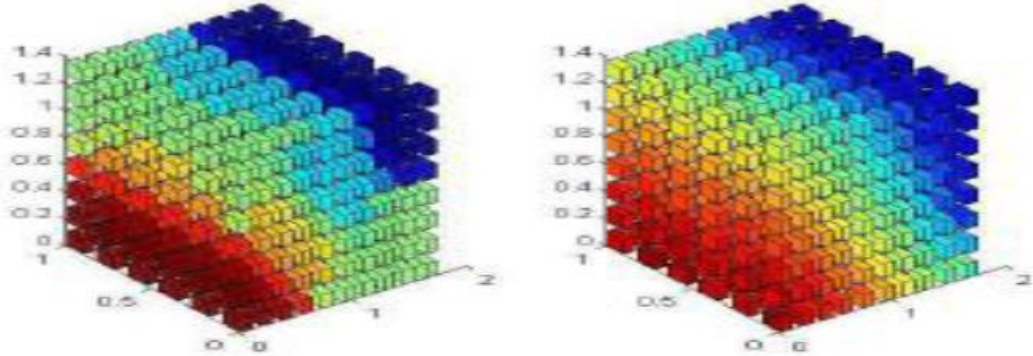


Figure 3: Real-time 3D ethanol (right) and acetic acid (left) concentration reconstruction (computed @ datasink) using a 4 w-nose deployment in the glass box experimental setup.

References

1. M. Kamionka, et al., Calibration of a multivariate gas sensing device for atmospheric pollution measurement, *Sens.Act. B Chem.* 18(2006) 323–327.
2. S. De Vito et al. Semi-Supervised Learning Techniques in Artificial Olfaction: A Novel Approach to Classification Problems and Drift Counteraction, *IEEE Sensors* vol.12, Issue 11, 2012, 3215-3224.
3. W. Tsujita, et al., Gas sensor network for air-pollution monitoring, *Sens. Actuators B: Chem.* 110 (2005) 304–311.
4. S. Bicelli et al. “Model and Experimental Characterization of the Dynamic Behavior of Low-Power Carbon Monoxide MOX Sensors Operated With Pulsed Temperature Profiles”, *IEEE Trans. Instrumentation and Measurement*, May, 2009, Vol. 58, N. 5, pp. 1324-1332.
5. S. De Vito et al., Wireless Sensor Networks for Distributed Chemical Sensing: Addressing Power Consumption Limits with On-Board Intelligence. *IEEE Sensors Journal*, Vol. 11, Issue 4, pp.947- 955.
6. S. De Vito et al., *Procedia Engineering*, Volume 25, 2011, Pages 84-87, ISSN 1877-7058, 10.1016/j.proeng.2011.12.021.
7. Achim J. Lilienthal, Amy Loutfi and Tom Duckett, Airborne Chemical Sensing with Mobile Robots. *Sensors*, 6, pp. 1616-1678 (2006).

CARBON-BASED NANOMATERIALS FOR GAS SENSING

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Abstract

Ammonia-gas-sensing characteristics for gold-decorated carbon-nanotube yarns (CNT yarns) at room temperature are presented. CNT yarns were fabricated from vertically aligned multiwalled carbon-nanotube forests [1]. The CNT yarns were first treated either with strong acid or in a pulsed direct-current plasma containing Ar and either oxygen or hydrogen. Au nanoparticles were subsequently deposited onto the surfaces of CNT yarns. The plasma treatment leads to surface modification resulting in dense and uniformly-distributed Au particles smaller than 3 nm along the lengths of CNT yarns. Nanocrystalline Au particle distributions, in the cases of untreated and acid treated CNT yarns, were sparse and the particle sizes were larger (10–20 nm). In all cases Au nanoparticles increased the sensitivity (measured as a change in resistance in a chemiresistor arrangement) to NH₃ by about a factor 10 in comparison to yarns with no Au. The lowest concentration of NH₃ that was detectable using this method was ~500 ppb. Plasma-treated and Au decorated samples showed stable, reproducible response and recovery [2].

When the carbon nanotube yarns were decorated with nanocrystalline Pd (Pd-MWCNTs) hydrogen was detected from 20 parts per million (ppm) and above in nitrogen at room temperature. With chemiresistors fabricated using a layer of Pt on Pd (Pt–Pd-MWCNTs), the lower limit of detection (LLD) was found to extend down to 5 ppm. It is shown that the observed response to hydrogen is a resultant of two mechanisms, namely, the formation of the hydrides of Pd and nanoscopic gap closing which leads to opposing changes in resistance in the composite yarns. In air, the LLD was found to be 2000 ppm for the Pd-MWCNT chemiresistor and 400 ppm for the Pt–Pd-MWCNT chemiresistor. The Pt–Pd-MWCNT chemiresistor showed excellent response and recovery characteristics in air. For Pd-MWCNT chemiresistor, the nanoscopic gap-closing mechanism became prominent at concentrations below ~1000 ppm and allowed the detection of hydrogen down to 200 ppm in air using negative changes in resistance [3].

Annealing at high temperatures and exposure to strong ultra violet light are the approaches used in the past for affecting the desorption of strongly bound gases such as ammonia (NH₃) and nitrogen dioxide (NO₂) from single wall carbon nanotubes (SWCNT) and graphene. These methods pose severe limitations in the development of devices which can operate in normal ambient conditions. The use of another gas which can influence the kinetics of desorption of gases already present on the SWCNTs has not been explored in detail. Here we show that the redistribution of substrate impurity states near Fermi Level, caused by the electrostatic forces of polar molecules like water, accelerates the desorption of gases bound on SWCNT. This phenomenon can be used to facilitate complete, rapid and non-destructive desorption of NO₂ and NH₃ molecules from SWCNT chemiresistors at room temperature.

Complete desorption of these gases were achieved within minutes instead of many hours as reported previously in the literature. The method provides a practical alternative for achieving recovery in CNT-based molecule detectors in air without the risk of degradation of the SWCNTs and their sensitive polymer composites which are used to achieve high sensitivity and selectivity [4].

Molecular doping and detection are in the forefront of graphene research, a topic of great interest in physical and material science. Molecules adsorb strongly on graphene leading to a change in electrical conductivity at room temperature. However, a common impediment for practical applications reported by all studies to date, is the excessively slow rate of desorption

of important reactive gases such as ammonia and nitrogen dioxide. Annealing at high temperatures, or exposure to strong ultra violet light in vacuum environment is employed to facilitate desorption of these gases. In this article, we show that the molecules adsorbed on graphene nanoflakes and on chemically-derived graphene-nanomesh flakes can be displaced rapidly at room temperature in air by the use of gaseous polar molecules such as water and ethanol. The mechanism for the desorption is proposed to arise from the electrostatic forces exerted by the polar molecules which uncouples the overlap between substrate defect states, molecule states and graphene states near the Fermi level. Using chemiresistors prepared from water-based dispersions of single-layer graphene on mesoporous alumina membranes, the study further shows that the edges of the graphene flakes (showing p-type response to NO₂ and NH₃) and the edges of graphene nanomesh structures (showing n-type response to NO₂ and NH₃) have enhanced sensitivity. The measured responses towards gases are comparable or better than any obtained using more sophisticated devices. The high sensitivity and rapid regeneration of the sensor at room temperature provides a clear advancement towards practical molecule detection using graphene-based materials [5].

References

1. L.K. Randeniya A. Bendavid P.J. Martin, and C. Tran, "Composite yarns of multiwalled carbon nanotubes with metallic electrical conductivity", *Small* **6**(16) (2010)1806-1811.
2. L.K. Randeniya, P.J. Martin, and A. Bendavid, "Ammonia sensing characteristics of carbon-nanotube yarns decorated with nanocrystalline gold", *Carbon*, **49** (2011) 5265-5270.
3. L.K. Randeniya, P.J. Martin and A. Bendavid, "Detection of hydrogen using multi-walled carbonnanotube yarns coated with nanocrystalline Pd and Pd/Pt layered structures", *Carbon* **50** (2012)1786-1792.
4. L.K. Randeniya and P.J. Martin "Removal of strongly bound gases from single wall carbon nanotubes without annealing or ultraviolet light exposure" *Carbon*, in press.
5. L.K. Randeniya, H. Shi, A.,S. Barnard, J. Fang, P.J. Martin and K. Ostrikov, "Harnessing the influence of reactive gases and defects on substrates for achieving complete cycle of room-temperature molecular sensing using graphene", *Small*, in press.

EMERGING HYBRID MATERIALS FOR AIR-POLLUTION MICROSENSORS*M. Bouvet, P. Gaudillat, J.-M. Suisse*

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Abstract

Interest in molecular materials has been driven in large part by their various and prosperous applications, especially in the domain of organic electronics, where they offer many advantages as well as alternative approaches. In the present review, we show how the chemical variability of phthalocyanines allowed to synthesize a broad range of hybrid materials. The combination of phthalocyanines or related derivatives with polymers or carbonaceous materials led to efficient chemical sensors. It is shown how the incorporation of macrocyclic molecules in hybrid materials highly modifies the structural and morphological characteristics of the materials. Rugosity, specific surface and porosity being key parameters in the analyte-sensing material interactions, these modifications highly improve the performance of chemical sensors. This is the reason why they are particularly promising materials for the development of new chemical sensors, associated with electrochemical, conductimetric or optical transducers.

The sensitivity can be generally improved by increasing the interaction between the material and the target analyte. It is the reason why sensitivity depends on morphological parameters of the sensing materials, namely the specific surface, rugosity, porosity, and the size of cristallites, which define the density of adsorption sites [1]. Selectivity depends directly on the choice of sensing materials that have to be adapted to the target species. Of course, it cannot be defined independently of the transduction mode, which is chosen as a function of the physical parameter that is modified by the analyte-sensing material interaction. Selectivity to a target species has to be considered for each particular application. Indeed, a sensor will be considered as selective in a given environment, but may be unselective in another one where an interfering species is present. Stability is the third main property required for sensors. At first, it supposed that the gas-sensing material interactions are reversible. Reversibility can be improved with sensing materials in the form of very thin and amorphous films. Indeed, in cristalline materials and in thick films, long exposure periods to a gas will induce an occupation of rather unaccessible sites, from which the adsorbed species may have difficulty getting out. It occurs when the adsorbed species diffuse deeply inside thick and/or cristalline films [1].

The covalent grafting on CNTs is the first possibility to increase their processability, starting from carboxylic acid or amino modified CNTs, for exemples, making them capable to react with amine or carboxylic acid groups-containing macrocycles, respectively [2,3] (Fig. 1). However, it highly modifies the electrical properties of materials. It is the reason why noncovalent functionalization is often preferred [4].

To overcome the too high cristallinity of some phthalocyanines can be achieved by combining them with polymers, by dissolution in a common solvent and deposited by solution processing, namely solvent-cast or spin-coating technics. The hydrophilicity of sensing materials can be adjusted by the composition of the polymer. Hybrid materials combining polypyrrole (PPy) with an ionic phthalocyanine, namely a sulfonated cobalt phthalocyanine (s-CoPc), as counteranion, were electrosynthesized at the surface of Pt electrodes [5,6]. It was shown that ionic macrocycles modify the morphology of the films, with smaller cristallites and lower rugosity compared to rather small anions like perchlorate or naphthalene sulfonate, as shown by optical topomicroscopy images (Fig. 2). s-CoPc provides hydrophilic properties to the blend, but it induces the conductivity variation only at very low humidity levels, between 0 and 20% of RH. At higher RH, the conductivity of PPy/s-CoPc varies only slightly (Fig.

3). Then, the response to ammonia (NH_3), in the range 20-100 ppm remains almost constant in a broad range of RH (20-80%).

The combination of phthalocyanines and porphyrins with carbonaceous materials or with polymers in hybrid materials offers the possibility to tune their physical properties, leading to chemical sensors with better performances compared to these prepared from a single component.

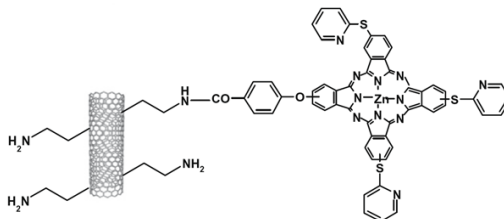


Figure 1. View of ZnPc chemically linked to SWCNT obtained by reaction of a carboxyphenoxy-substituted ZnPc with an amine functionalized SWCNT (after [3]).

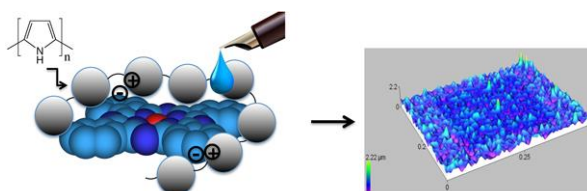


Figure 2. Optical topomicroscopy image of an electrodeposited film of sulfonatedCoPc/polypyrrole and a schematic view of the coulombic interactions between the two components (modified from [5]).

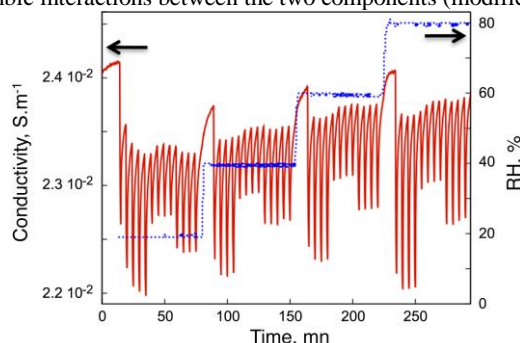


Figure 3. Response of a PPy/s-CoPc hybrid material to ammonia in exposure/recovery cycles (1 / 4 min.) at successively 90, 25 and 45 ppm, under various relative humidity levels (20, 40, 60 and 80 RH %) (adapted from [5]).

References

1. J. D. Wright "Gas adsorption on phthalocyanines and its effects on electrical properties" *Prog. Surf. Sci.* **31** (1989) 1–60.
2. J. H. Zagal, S. Griveau, M. Santander-Nelli, S. Gutierrez Granados, F. Bedioui "Carbon nanotubes and metalloporphyrins and metallophthalocyanines-based materials for electroanalysis" *J. Porphyrins Phthalocyanines* **16** (2012) 713–740.
3. W. Chidawanyika, T. Nyokong "Characterization of amine-functionalized single-walled carbon nanotube-low symmetry phthalocyanine conjugates" *Carbon* **48** (2010) 2831–2838.
4. M. Penza, R. Rossi, M. Alvisi, M. A. Signore, E. Serra, R. Paolesse, A. D'Amico, C. Di Natale, "Metalloporphyrins-modified carbon nanotubes networked films-based chemical sensors for enhanced gas sensitivity", *Sensors and Actuators B* **144** (2010) 387-394.
5. T. Sizun, T. Patois, M. Bouvet, B. Lakard, "Microstructured electrodeposited polypyrrole-phthalocyanine hybrid material, from morphology to ammonia sensing", *J. Mater. Chem.* **22** (2012) 25246-25253.
6. T. Sizun, M. Bouvet, J.-M. Suisse, "Humidity effect on ammonia sensing properties of substituted and unsubstituted cobalt phthalocyanines", *Talanta* **97** (2012) 318-324.

CONDUCTING POLYMER SENSOR ARRAYS FOR AIR-QUALITY MONITORING APPLICATIONS

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Abstract

Conducting polymers have several advantages for gas sensor applications. They are relatively low cost materials, available in various molecular structures, sensitive to different organic vapours. Their fabrication is quite simple and the film properties can be controlled by electrochemical methods. Because they can operate at room temperature, there are significant advantages in applications where low power requirements are important. The synthesis of conducting polymers can be carried out chemically, by adding oxidant to monomer in aqueous or organic solution, or electrochemically by applying constant voltage (potentiostatic), constant current (amperostatic), or potentiodynamic (cyclic voltammetry). We have investigated a number of materials for gas sensing. These include polythiophenes bearing alkoxy side chains which have good conductance stability. This is because oxygen in the alkoxy chain donates electrons to thiophene rings and the void between the chains accommodates the dopant ion.

Other materials of interest include polyanilines. These are of great importance to us because they display high sensitivity to ammonia. We are interested in sensing ammonia in food, agriculture and water quality applications. Solution-processable conducting polyaniline formulations were successfully prepared using multifunctional dopants: sulfosuccinic acid and 4-sulfophthalic acid, in *n*-methylpyrrolidone as solvent. The doped structures were characterised by UV-Vis spectroscopy and X-ray photoelectron spectroscopy, and the presence of polarons/bipolarons were confirmed which is indicative of the complete conversion of emeraldine base to emeraldine salt form of polyaniline. The doped mixtures were then used to make hybrid composites of polyaniline and carbon nanoparticles. Surface-treated carbon nanoparticles showed promising features in making hybrid nanocomposites with fine dispersion and uniform distribution of nanoparticles in the polyaniline matrix, without deteriorating the electrical properties. AFM images showed efficient dispersion of particles in nanometre ranges. Flexible plastic substrates, Kapton® and PEN, incorporating interdigitated gold electrodes were coated with the hybrid nanocomposites and were used for ammonia sensing measurements. Highly sensitive, rapid and recoverable responses in sub-ppm concentration of ammonia, produced by a permeation tube, were observed when a sub-miniature heater was used to keep the sensors at 80 °C. Using spin coating instead of dip coating enhanced the sensitivity about 2 times. The sensitivity of the hybrid nanocomposites was compared to that of a commercial MOS ammonia sensor. The hybrid nanocomposites show higher sensitivities while consuming less power due to their lower operating temperature. Effects of temperature and substrate material on sensing behaviour were investigated. These materials show great potential in order to be used in real-time ammonia sensing applications.

Results

Sensors made from hybrid composites of doped polyaniline and carbon black were made on plastic substrates with interdigitated electrodes. Figure 1 shows the response of a dip-coated sensor from the 1wt.% SSA-doped PANI/CB mixture on flexible Kapton® substrate toward 3 different concentrations of ammonia vapour. The heater keeps the sensor temperature at 80 °C. The response is recorded as the relative resistance change

$$\frac{R_{\max} - R_b}{R_b} \times 100\% \quad \text{Eq.1}$$

where R_{\max} and R_b are the maximum resistance during exposure and baseline resistance of the sensor, respectively. As can be seen, the responses are fast, recoverable and repeatable for all three concentrations. The exposure time is equal in all three cases; however the recovery time (time needed for the sensor to recover back to its baseline resistance value) varies with the concentration; as the concentration increases from 340 ppb to 1150 ppb, the recovery time increases from about 10 min to 15 min.

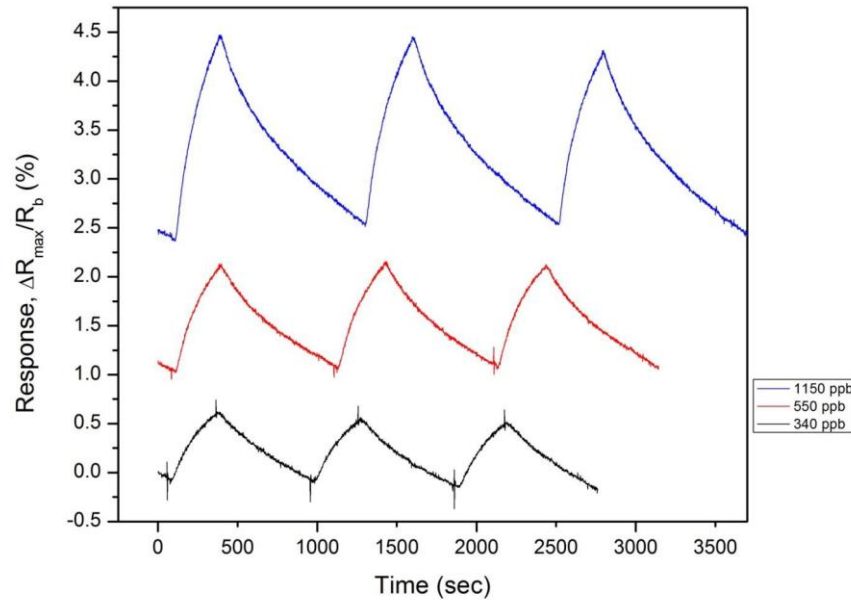


Figure 1 Response of a SSA-PANI/CB dip coated sensor on Kapton® toward 340, 550 and 1150 ppb ammonia at 80 °C. In all cases exposure time is 300 s (5 min), and the sensor has been given enough time to recover to the R_b .

To better investigate the sensing performance of our sensor, we compared the sensing results from our sensor with a successful commercial MOS ammonia sensor from Synkera Technologies, Inc. (USA). Sensors were placed in series and exposed to an ascending concentration of ammonia vapour from 425 ppb to 2.25 ppm. The exposure and recovery time were fixed to 180 and 300 sec, respectively. The results are shown in Figure 2. Clearly, the hybrid sensor outperforms the commercial MOS sensor in terms of response intensity and sensitivity. However, the MOS sensor is faster both in response and recovery. Since the recovery of the hybrid sensor is not complete in 300 sec (recovery period), a significant baseline drift is observed. This issue can be solved easily by dedicating more time for recovery to the polymeric sensor, as can be seen in Figure 1. Nevertheless, the power consumption of the hybrid sensor is much lower than the MOS sensor, due to their significantly lower operating temperature

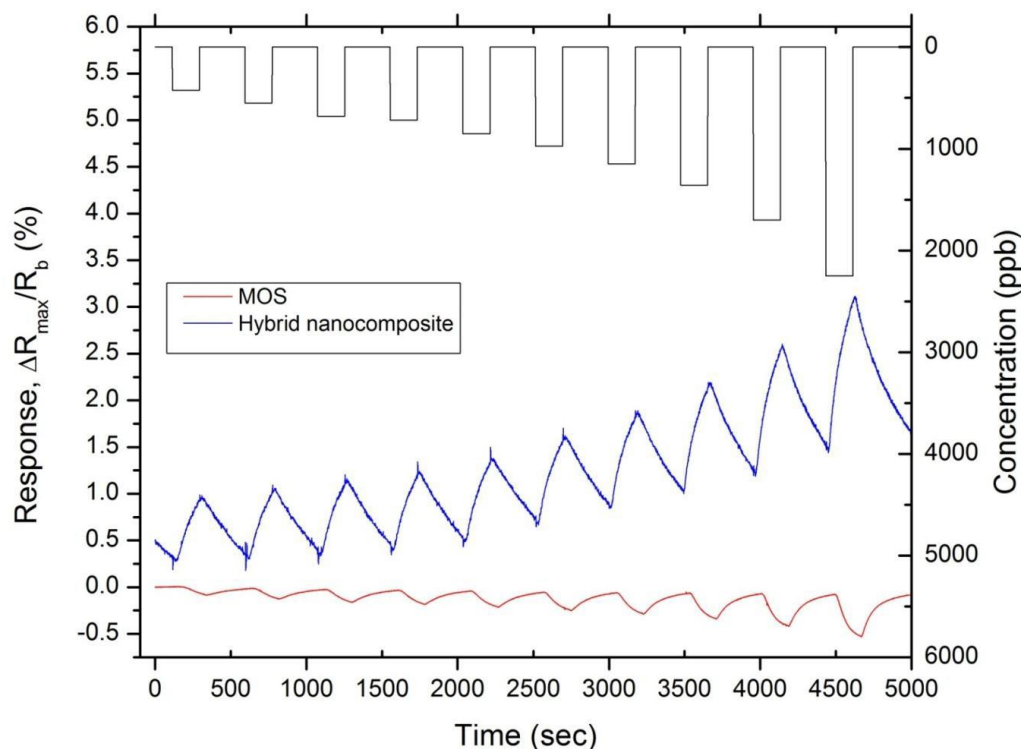


Figure 2 Ammonia sensing behaviour of hybrid SSA-doped PANI/CB sensor (dip coated on Kapton®; blue line) and Synkera's MOS ammonia sensor (red line). The hybrid sensor kept at 80 °C with the sub-miniature ceramic heater. Ammonia concentrations are indicated as bar graphs (black line) for each measurement. Exposure and recovery durations are 3 and 5 min, respectively.

Conclusion

Solution-processable conductive polyaniline formulations have been successfully prepared using 'counter-ion induced processability' concept. Two multifunctional protonating agents, namely sulfosuccinic acid and 4-sulfophthalic acid, were employed which have two functional group types: a sulfonic acid group which dopes polyaniline (converting non-conducting emeraldine base to electrically conducting emeraldine salt) and carboxylic acid groups which interact with the solvent molecules and make the complex soluble in aprotic solvents such as NMP. Hybrid nanocomposites of polyaniline and surface-modified carbon black particles were successfully made using the doped-PANI solutions in NMP. Flexible Kapton® and PEN substrates incorporating gold interdigitated electrodes were coated with thin layers of the hybrid nanocomposites, and were used for ammonia sensing measurements in sub-ppm range. Sensors were operated at an elevated temperature to enhance the recovery. The responses are fast, recoverable and repeatable in the concentration range studied between about 200 ppb to 2 ppm.

Acknowledgement: This work was supported by EU project FlexSMELL 238454 FP7-PEOPLE-ITN-2008.

CO₂ GAS SENSOR BASED ON MIS STRUCTURE WITH LaF₃ LAYER

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The aim of this research is to find a CO₂-sensor with sufficiently high response to CO₂ concentrations in a range of some hundreds ppm, with short response and recovery time, working at room temperature, which could be applied, for example, in air conditioning. The sensor investigated in this work is based on MIS (MIES) structure with fluorine conducting LaF₃ layer (Fig. 1).

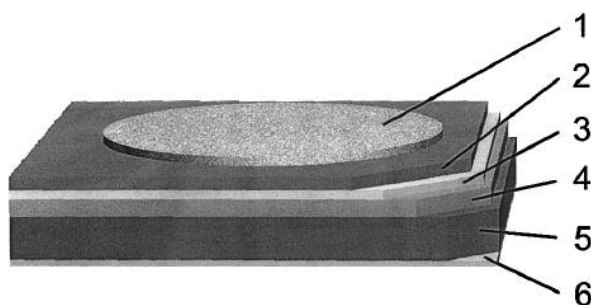


Figure 1: Scheme of MEIS gas sensor. (1) platinum gate electrode; (2) LaF₃ solid electrolyte layer; (3) Si₃N₄ layer; (4) SiO₂ insulation; (5) silicon substrate; (6) Al ohmic contact.

Earlier, we started the investigations of MIS devices with solid electrolyte layer (that is, MEIS devices). In [1], we reported the results obtained with proton and CO₃²⁻ conducting solid electrolyte layer. These MEIS structures are sensitive to CO₂, however further improvement of gas sensors is necessary.

In our study of MEIS sensors of F₂ and HF with layer of LaF₃ [2], we found that the aging of the device in air is due to the formation of lanthanum fluorocarbonate layer. This layer can be easily decomposed by heating the sensor up to 150 – 200⁰C. On the other hand, N.Barsan et al. [3,4] recently reported the results of the application of lanthanum hydroxocarbonate as a material of CO₂ resistive sensor. However, in [3,4] it was noted that the resistance of sensing layer is too high (~10¹⁰ Ohm) and the response time is too long (>1 hour) for practical application. We used the results of [2-4] as a starting point of our research. The idea is the application of lanthanum oxyfluoride layer, which adsorbs easily carbon dioxide with the formation of lanthanum fluorocarbonate, as a sensing layer of MEIS structure. In this case, high resistance of sensing material is not important, because the measured parameter is capacitance of MEIS capacitor. The sensor was fabricated by thermal deposition of LaF₃ (200 nm) in high vacuum. Platinum gate (30 nm thick) was deposited by sputtering in Ar atmosphere. Total structure was therefore Al/Si/SiO₂/Si₃N₄/LaF₃/Pt [2]. Measurements of capacitance were performed at AC voltage frequency of 10 kHz and amplitude of 10 mV.

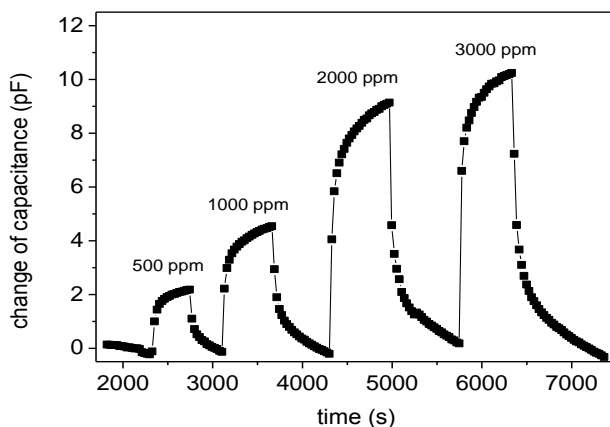


Figure 2: The responses to different CO₂ concentrations at constant humidity equal to 60 % before sensor activation.

The response of MEIS structure to CO₂ concentrations was measured in two modes: (1) the response of the sensor “as prepared”, without any additional treatment of the MEIS capacitor; (2) the response after activation consisting in 10 min. heating the sensor on air at temperature of 150–300⁰C. This last procedure leads to the formation of lanthanum oxyfluoride on the surface of LaF₃.

Measurement of sensor response was performed in humid carrier air with relative humidity of 40, 60, and 80% with CO₂ concentrations in a range 300–3000 ppm, most interesting for practical application.

Fig. 2 shows room temperature response of the sensor without any additional treatment to CO₂ concentrations at 60% RH.

An increase in relative humidity of carrier gas makes shorter the response time of the sensor. Fig. 3 represents the sensor response to CO₂ concentrations at relative humidity of 80%. The response time ($\tau_{0,63}$) is equal to about 50 s.

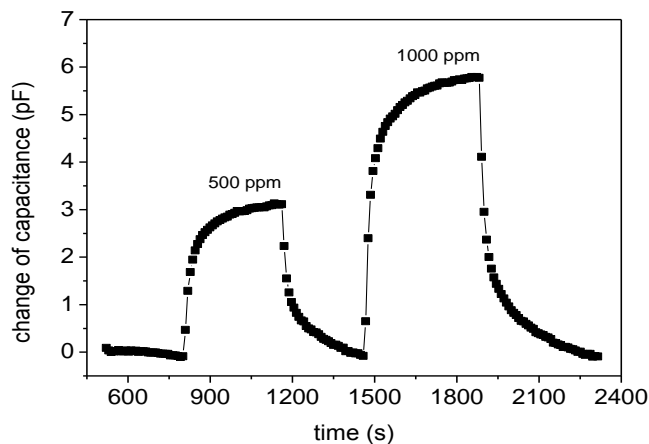


Figure 3: The responses to different CO₂ concentrations at constant relative humidity equal to 80 % before sensor activation.

In accordance with suggested mechanism, 10 min. heating at 300⁰C increases the response by a factor of 2 (Fig. 4). These measurements (blue line) were performed approximately 2 hours after the sensor activation.

Higher sensitivity was obtained, if the measurements were carried out immediately after the activation of the MEIS capacitor. The sensor response increases in this case approximately by a factor of 10.

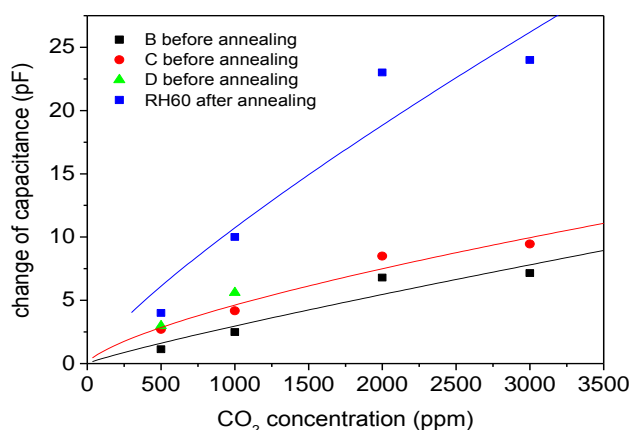


Figure 4: Change of capacitance as a function of CO₂ concentration and allometric fits according to a power law $y=ax^b$ (solid lines). Black, red, and green signs – the measurements were performed with sensor without activation (heating at 300⁰C for 10 min). Blue signs – sensor after activation.

Therefore, the application of “activated” MEIS gas sensor with a layer of fluorine conducting solid electrolyte LaF₃ seems to be very promising for the measurement of CO₂ concentrations in a range from atmospheric background (300 ppm) to MPC (2000 ppm). The sensing

mechanism consists in the reversible formation of lanthanum fluorocarbonate on the surface of solid electrolyte layer.

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REFERENCES:

- [1] A.E.Varfolomeev, I.R.Shandova, A.S.Lagutin, A.A.Vasiliev*, A.V.Pisareva, A.V.Levchenko, Yu.A.Dobrovolskiy. "Sensor of Carbon Dioxide Based on MIS Structure with Solid Electrolyte Layer". *Procedia Engineering*, vol. 47, pp. 170-173, 2012.
- [2] L.Bartolomaus, A.A.Vasiliev, W.Moritz. "Semiconductor sensors for fluorine detection - Optimization for low and high concentrations". *Sensors and Actuators, B*, vol. 65, pp. 270-272, 2000.
- [3] A.Haensch, D.Koziej, M.Niederberger, N.Barsan, U.Weimar. "Rare earth oxycarbonates as a material class for chemoresistive CO₂ gas sensors", *Procedia Engineering*, vol. 5, pp. 139-142, 2010.
- [4] A.Haensch, D.Borowski, N.Barsan, D.Koziej, M.Niederberger, U.Weimar. "Faster response times of rare-earth oxycarbonate based CO₂ sensors and another readout strategy for real-world applications". *Procedia Engineering*, vol. 25, pp. 1429-1432, 2011.

DETECTION OF LOW CONCENTRATIONS OF VOLATILE ORGANIC COMPOUNDS WITH SiC-FIELD EFFECT TRANSISTORS

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Summary

In this work the suitability of gas sensitive silicon carbide field effect transistors (SiC-FETs) for the detection of volatile organic compounds (VOCs) in the ppb range was studied. As typical VOCs benzene, naphthalene and formaldehyde were chosen. It was found that both platinum and iridium gate SiC-FETs are able to detect VOCs down to a few ppb. The highest sensitivity was found for naphthalene but 1 ppb of benzene is still detectable. Hence, they are suitable candidates to measure VOCs, e.g. in indoor air applications.

Motivation

Indoor air quality has become a major issue in recent years since people spend most of their time indoors where fresh air exchange is increasingly limited to reduce energy consumption. The result is often the so called sick building syndrome. Besides the level of carbon dioxide the quality of the air is strongly affected by volatile organic compounds (VOCs) which pose a serious health risk [1,2]. Some of them are increasing the risk for cancer, like benzene. Thus, detecting VOCs, respectively the total amount of VOCs (TVOCs) with high-sensitive and low cost gas sensor systems is an inquired demand. However, this is a challenging task since the concentrations of VOCs to be detected are very low. Gas sensitive SiC-FETs have been studied for many years and were successfully used in various applications, mostly for measuring exhaust gases [3,4]. In this work their suitability for VOC detection in the ppb range was studied.

Results

For all measurements, n-channel depletion type SiC-FETs with 25 nm thick, porous platinum and 30 nm thick, porous iridium gates were used (Fig. 1a) [5]. The sensor dies are glued on ceramic heaters together with a Pt-100 temperature sensor to determine the actual sensor temperature. The heaters with the sensors are mounted on a TO-8 header (Fig. 1b). The FETs are operated in a constant current mode (14 μ A for the iridium and 45 μ A for the platinum gate FET) and the voltage drop is measured. The baseline of the iridium FET was adjusted by applying a gate bias V_G of 2 V.

Benzene, naphthalene and formaldehyde were chosen as typical VOCs. The first two gases are supplied by permeation ovens (VICI Dynacalibrator 150) and formaldehyde was used from a gas bottle together with a diluting apparatus to create ppb concentrations of the test gas. The carrier gas for all measurements was dry synthetic air.

Both types of gas sensitive FETs are suitable to detect ppb-level of VOCs. Detection limits of a few ppb for benzene and naphthalene were found for the platinum gate SiC-FET (Fig. 2a). The iridium gate SiC-FET shows a high sensitivity to formaldehyde and concentrations below 100 ppb can still be detected (Fig. 2b).

Thus, gas sensitive field effect transistors based on silicon carbide are suitable to measure VOCs in the relevant concentration range. By combining different sensor materials or by making use of dynamic operating modes [4] high selectivity vs. hazardous VOCs can be achieved to realize optimized ventilation scenarios for indoor applications.

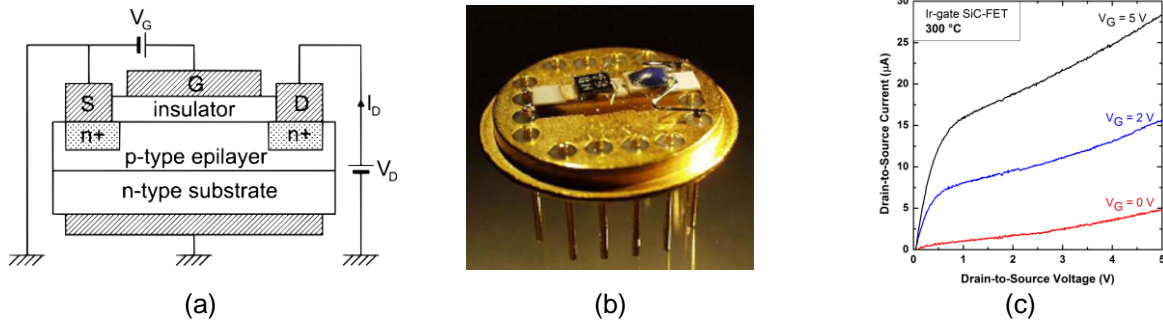


Figure 1. Schematic cross-sectional view of the gas sensitive SiC-FET (a), sensor die with ceramic heater mounted on TO-8 header (b), and typical IV curve of an Ir-gate SiC-FET at 300 °C in synthetic air (c).

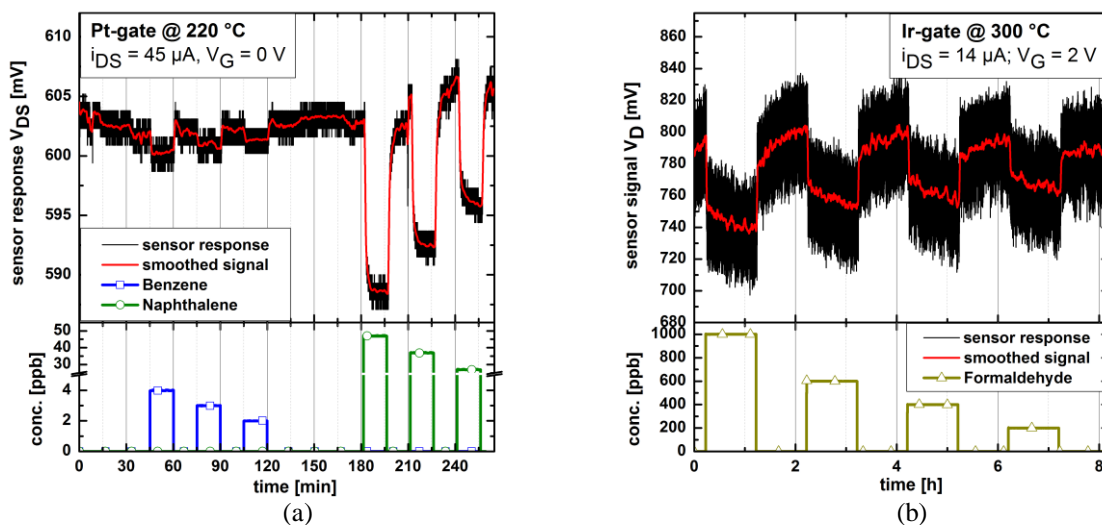


Figure 2. Sensor response of a Pt-gate SiC-FET to benzene and naphthalene at 220 °C and zero gate bias, $V_G = 0$ V (a), and sensor response of an Ir-gate SiC-FET to formaldehyde at 300 °C and $V_G = 2$ V in order to adjust the baseline (b). The sensor responses were smoothed by a moving average filter with a span of 500 points.

Acknowledgement

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References

1. D.A. Sarigiannis, S.P. Karakitsios, A. Gotti, I.L. Liakos, and A. Katsoyiannis, "Exposure to major volatile organic compounds and carbonyls in European indoor environments and associated health risk," *Environmental International*, vol. 37, 2011, pp. 74-765.
2. D.H. Do, H. Van Langenhove, C. Walgraeve, S.F. Hayleeyesus, P. De Wispelaere, J. Dewulf, and K. Demeestere, "Volatile organic compounds in an urban environment: a comparison among Belgium, Vietnam and Ethiopia," *Intern. J. Environ. Anal. Chem.*, vol. 93, no. 3, 2013, pp. 298-314.
3. I. Lundström, H. Sundgren, F. Winqvist, M. Eriksson, C. Krantz-Rülcker, and A. Lloyd Spetz, "Twenty-five years of field effect gas sensor research in Linköping," *Sens. Actuators B*, vol. 121, no. 1, 2007, pp. 247-262.
4. C. Bur, P. Reimann, M. Andersson, A. Lloyd Spetz, and A. Schütze, "Increasing the selectivity of Pt-gate SiC field effect gas sensors by dynamic temperature modulation," *IEEE Sens. Journal*, vol. 12, no. 6, 2012, pp. 1906-1913.
5. M. Andersson, R. Pearce, and A. Lloyd Spetz, "New generation SiC based field effect transistor gas sensors," *Sens. Actuators B*, vol. 179, 2013, pp. 95-106.

ENSEMBLE AVERAGING FOR LOW-POWER GAS DETECTION USING INDIVIDUAL CARBON NANOTUBES

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Abstract

Single-walled carbon nanotubes (SWCNTs) are candidates for miniaturized and low power gas sensors. They can operate as chemical transducers utilizing various working principles, such as chemiresistors, chemicapacitors, chemtransistors (ChemFETs), mechanical structures (SAW, M(N)EMS), calorimetric sensors, ionization sensors, etc. [1]. In this work, we focus on NO₂ gas sensors utilizing *individual* SWCNTs as the active (sensing) part of field effect transistors (CNFETs) [2, 3] because both the size and the power consumption can be reduced compared to other configurations such as mat or forest-based CNT sensors. To contribute ongoing debate about nanotube gas sensor design, here we show the effect of ensemble averaging of sensors based on individual nanotubes, and compare it to the performance of sparse nanotube networks. Although network-sensors show a superior signal-to-noise ratio compared to individual nanotube sensors, they also consume higher power. However, we show from our measurements of ensemble averaging of individual tube sensors, a comparable performance may be achieved at only 40% of the power consumption of the mat sensors.

Experimental

For mat-sensors, a network of nanotubes was grown using the same catalyst and growth conditions, followed by a patterning of the device channel by O₂-plasma at 100 W for 30s. Metal contacts were then patterned by lift-off. Single-nanotube sensors were fabricated by a statistical approach with approximately 40% yield. A detailed description of this approach can be found in [4]. In short, nanotubes were grown at a known density from defined catalyst islands directly on the target substrate, which is a highly-doped silicon wafer with 70 nm SiO₂ as gate dielectric. The contact geometry was optimized to maximize the yield of single-nanotube devices. In both cases, 40 nm Al₂O₃ was deposited to passivate the contacts followed by a channel opening to expose the nanotubes to the environment [5].

Results

Figure 1 shows the sketch of the device design, AFM image of part of the SWCNT network and the CNFET response signal obtained after exposing the sensor to 1 ppm of NO₂ gas in synthetic dry air at ambient temperature.

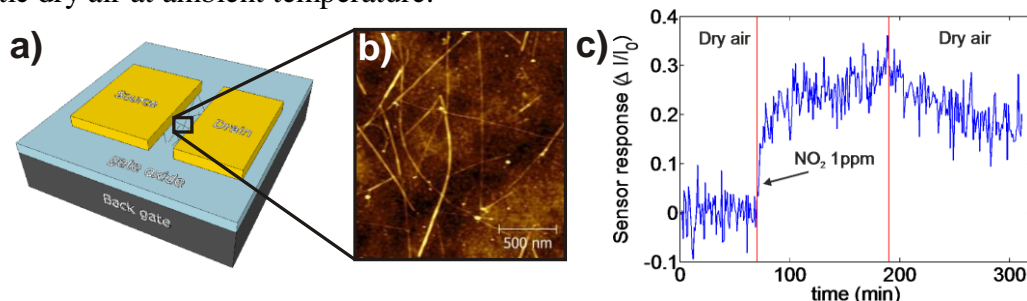


Figure 1. Mat sensor fabricated using a simple photolithography approach. a) Sketch of device design, b) AFM image of nanotube network between source & drain electrodes, c) sensor response to 1ppm NO₂ exposure.

The power consumption of the mat sensor in typical operation is about 500 nW. The ‘signal-to-noise’ ratio of this sensor at 1ppm can be defined as $SNR = \langle S_{on} \rangle / \sigma_{off}$ where σ_{off} is the

noise in the off state and $\langle S_{on} \rangle$ is the steady state response to NO_2 . For this sensor, the SNR is about 7.5, with an active sensing window of $150 \mu\text{m} \times 10 \mu\text{m}$.

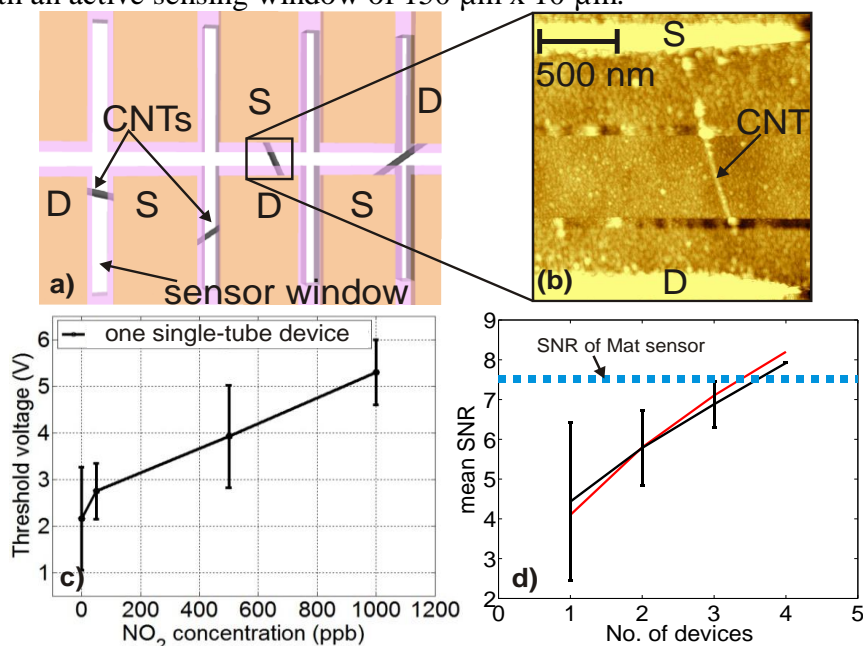


Figure 2. a) Schematic of a single-nanotube sensor array b) AFM image of a single sensor device. The nanotube is visible in the open window. c) sensor response of one device to various concentrations of NO_2 . d) Signal-to-noise ratio as a function of the number of devices in the ensemble. The red line indicates a \sqrt{N} trend. For reference, the SNR of the mat sensor is plotted. It is seen that already for 4 devices, the SNR of the ensemble exceeds the SNR of the mat sensors.

For comparison, we measured an array of four individual-tube sensors (figure 2). The sensor response of a single sensor can be relatively noisy, as seen in figure 2c. However, the noise in different devices is uncorrelated (not shown) and can be averaged to improve the SNR, as shown in figure 2d. It is seen that the SNR follows a \sqrt{N} trend (N : number of devices). From this trend, we observe that the SNR from ensemble averaging already exceeds that of the nanotube mat sensor for 4 devices. As a comparison, the active device area in the mat sensor is around $150 \mu\text{m} \times 10 \mu\text{m}$, which is expected to contain approximately 2000 nanotubes. Also, if we assume that the power consumption from each individually contacted nanotube is about 50 nW, the power consumption to achieve the mat-equivalent SNR is about 200 nW, which is significantly lower than the mat sensor (500 nW). This indicates that ensemble-averaging of single-tube sensor arrays may be advantageous over mat sensors in low-power applications.

Acknowledgement

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References

7. Y. Wang, J. T. W. Yeow, "A review of carbon nanotubes-based sensors", *Journal of Sensors*, (2009), 1-24.
8. J. Kong, N. R. Franklin, Ch. Zhou, M. G. Chapline, S. Peng, K. Cho, H. Dai, "Nanotube Molecular Wires as Chemical Sensors", *Science*, **287** (2000) 622-625.
9. M. Mattmann, C. Roman, T. Helbling, D. Bechstein, L. Durrer, R. Pohle, M. Fleischer and C. Hierold, "Pulsed gate sweep strategies for hysteresis reduction in carbon nanotube transistors for low concentration NO_2 gas detection", *Nanotechnology*, **21** (2010) 185501-9.
10. K. Chikkadi, C. Roman, L. Durrer, T. Suess, R. Pohle, C. Hierold, "Scalable fabrication of individual SWNT chem-FETs for gas sensing", *Procedia Engineering*, **47** (2012), 1374-1377.
11. M. Mattmann, T. Helbling, L. Durrer, C. Hierold, R. Pohle, M. Fleischer, "Sub-ppm NO_2 detection by Al_2O_3 contact passivated carbon nanotube field effect transistors", *Applied Physics Letters*, **94** (2009), 183502.

OVERVIEW OF ENVIRONMENTAL MEASUREMENTS: ATMOSPHERIC POLLUTION

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Abstract

Air pollution due to airborne particulate matter is a major environmental problem. Several urban and industrial areas in Europe are not capable of meeting the implemented EU standards for particulate matter. A better understanding of the causes of the limit exceedances, and not just monitoring ambient air pollutant concentrations, is needed. Competent air quality management is required in order to ensure compliance with the limit values and that the consequences of poor air quality are controlled and minimized.

Air pollution is a trans-boundary, multi-effect environmental problem that damages human health and the environment. The latest World Health Organisation (WHO) health and environment progress report for Europe states that "urban air pollution, especially particulate matter, causes significant health problems throughout the region, reducing the life expectancy of residents of more polluted areas by over one year". In the same vein, the European Environment Agency (EEA) latest State of the Environment Report (SOER2010) shows that exposure to particulate matter (PM) and ozone (O₃) remains of major environment-related health concern, linked to a significant loss of life expectancy, acute and chronic respiratory and cardiovascular effects, impaired lung development in children, and reduced birth weight.

In Spain, due to the strong climatic contrasts found across the different regions, from the continental and commonly mountainous interior to the Mediterranean and Atlantic coastlines and archipelagos (Canaries and Balearics), the composition and seasonal patterns of atmospheric particulate pollutants in urban areas of these regions can vary significantly. The factors controlling the variations of ambient air PM levels are of particular concern, not least because European Directive 1999/30/CE is considerably more restrictive than that previously established in Spain, requiring a much greater control on anthropogenic emissions. PM₁₀ levels in Spain contain a high proportion of resuspended natural and anthropogenic particles (Querol et al., 2004a).

The location of monitoring stations in the different EU state members is based on different strategies designed by each country, so that the number of stations in rural, urban, traffic or industrial sites varies greatly. According to Airbase data from 2001 to 2002 (<http://air-climate.eionet.eu.int/>), in Spain between 70-80% of the monitoring sites are located in hotspots, while in other EU state Members the average is 40-45%, although the average can be lower than 16% in some cases. As an obvious result of this, Spain, with a higher proportion of traffic and industrial hotspots monitoring sites, will present average annual PM₁₀ levels and number of exceedances of the daily limit value higher than those countries with more rural and urban background monitoring sites. This difference is attributable to the fact that the monitoring of air quality in Spain was initially focussed on the control of maximum exposure levels in urban environments, this explaining why the measuring sites were located in hotspots (i.e. places with a very high level of PM such as those close to heavy traffic and industrial emissions). The new directive, however, tries to evaluate the level of PM to which a representative population of 250,000 inhabitants is exposed. Nevertheless, the new PM_{2.5} concentration cap is relatively permissive compared with the US PM_{2.5} limit value, although

the cap value applies also for hotspots. With these current challenges and changes to European pollution law in mind (Putaud et al., 2004), this paper presents a summary of the results obtained from the PM pollution data collected over a period of 6 years (1999-2005) from a wide range of sites across Spain, greatly increasing the database used in previous investigations (Querol et al., 2004a) and better illustrating the factors controlling the flux of particulate matter across the country.

In this work we review the main air quality problems in Spanish cities (NO₂ and PM), as well as the most frequent instrumentation used to characterise atmospheric pollution episodes. We assess the origin and sources of pollution, as well as the need for new sensors and monitoring techniques to enable us to maximise the spatial and temporal coverage of environmental measurements.

AIR QUALITY MONITORING PORTABLE SENSOR SYSTEM

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Abstract

In the ENEA center of Brindisi a portable gas sensor system called NASUS IV based on solid state gas sensors was builded. This system is the last result of our researches in the area of tiny and portable system building for air quality control based on solid state sensors. The main goal of the system designed and builded in our laboratory is the development of an hand held device in order to detect some pollutant gases such as CO, SO₂, NO₂ and H₂S. The most interesting features of this system can be summarized as follows:

- Hand held device (high portability degree)
- Fully remote operated via GSM/GPRS network
- Powered by Li-Ion battery or electrical energy network or solar cells systems
- Data logging by means of SD card memory inside the device
- PC interfacing for data downloading

Nasus IV is formed by four modules, or better, by four PCBs: the main module, the sensor module, the wireless module and the power module. The first three modules are packed in the same hand held case, but the power module is arranged in a separate case as shown in figure 1 and 2. The main module is in charge of managing the communications with the wireless module and with the PC via USB port, as well as, driving the local display, driving the mini-joystick (which is one of the input system, but not the only) and driving the SD card memory. On the sensor module are arranged six sensors: a temperature sensor, an humidity sensors and four electrochemical solid state gas sensors. The wireless module allows to remote control the device by means of commands inside an SMS sended from a mobile phone which will get the SMS answer returning from NASUS IV. Furthermore it can send e-mails containing any sensor data requested by the remote end user mobile phone. The power module provides to charge the battery inside NASUS IV, moreover it performs a smart management of the available power sources: network electricity or solar energy, giving priority to the solar one, whether possible. Currently, the sensors onboard NASUS IV are the electrochemical type sensors for the detection of CO, SO₂,NO₂ and H₂S provided by Alphasense LTD. We decided to test those electrochemical type sensors inside our device because of their interesting features such as, for example, very low power consumption, small dimensions, good sensitivity and improved response to interfering gases.

In order to test this machine in our laboratory under conditions as much as similar to the real situations, we employed a wide gas chamber provided by an input and an output pipe. The test gas is injected in the input one, while the output pipe allows the gas mixture to flow out. In this way we can create an environment containing a steady concentration of various type of gases to be tested.

We put NASUS IV in the previously described chamber and we performed several tests with different kind of gases. In the figure 3 and 4 is shown the main results of these tests: in these picture is represented the response of two sensors onboard NASUS IV machine to CO, NO₂ and H₂S gases.

Future works concern about the employment of NASUS IV in the real environment by performing experimental campaign in collaboration with ARPA-Puglia, which will provide in-field fixed stations in order to compare the performance of our machine with analytical gas analyzers. Moreover, at the same time, we are planning to design a new hand held system by

which we are going to test a new electrochemical gas sensor type having a more improved cross-sensitivity response and an improved sensitivity to very low gas concentrations.



Figure 1: Nasus IV machine

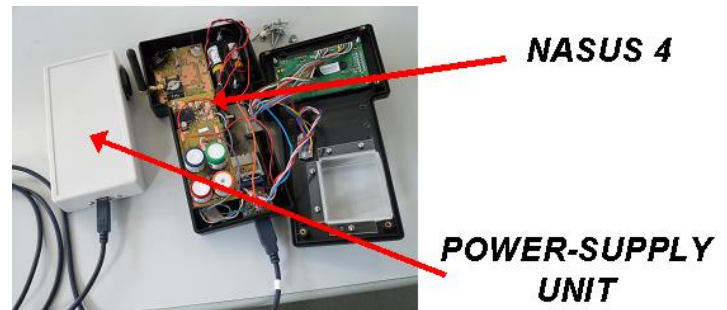


Figure 2: inside Nasus IV

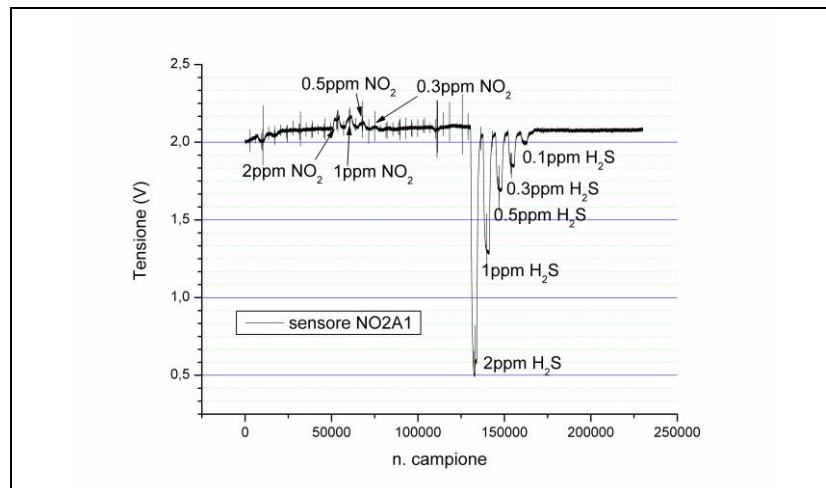


Figure 3: H₂S response

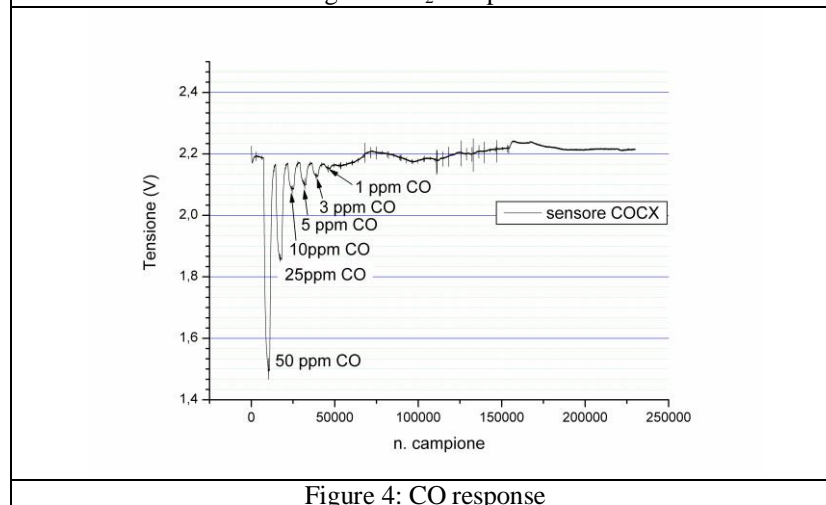


Figure 4: CO response

EMISSION MONITORING AND CONTROL BY GAS AND PARTICLE SENSORS FOR CLEAN ENVIRONMENT

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Summary

Due to environmental and health aspects it is important to measure and control toxic gases like ammonia and sulphur dioxide as well as particulate matter, PM, even at very low concentrations. We present an improved version of silicon carbide based field effect transistor gas sensors possible to tailor for specific gas molecules and the development of sensors for detection of concentration, and content of particles.

Motivation

Industry, power plants and traffic constitute some of the pollution sources of toxic gases and (nano)particles. Increasing awareness of the impact of toxic gases and particulate matter on the environment and our health is the driving forces for development of both gas and particle sensors for monitoring and control purposes. Chemical sensors have to be developed for every special application, since the background gas composition influences the sensor response. Selective and low level detection of two toxic gases, ammonia and sulphur, are demonstrated for power plant control application using a new design of the SiC-FET gas sensor technology [1] in temperature cycled mode with advanced data processing and evaluation [2]. Particles, especially nanosized, may penetrate lung tissue or directly enter the body through the skin and cause damage on vital organs like the heart and the brain. The toxic effect of particles is influenced of several parameters like their size, shape and content. Heating particles to a high temperature (up to 800°C) and measuring the emissions by gas sensors seems like a viable approach to detect content of particles and for development of fingerprint detection of particles [3]. Interdigital electrode, IDE, sensors are also developed for impedance spectroscopy with potential to detect concentration and size and eventually type of particles, while simple resistance measurements by IDEs can be used to detect the presence of particles [3].

Results

The current voltage characteristics of a depletion type n-channel SiC-FETs with 25 nm Ir as porous gate material operated at 300°C has been fine tuned to detect ammonia from a certain pre-set lower level in an atmosphere of low oxygen and rather high CO concentration (Fig. 1). Low oxygen concentration and somewhat higher CO level is the valid operation mode of power plants today, since this facilitates lower nitric oxide levels.

The SiC-FET sensor with 20nm Pt as porous gate material is also used for detection of sulphur dioxide in power plants. Temperature cycling mode and advanced data evaluation enables sulphur dioxide detection below 20 ppm in a varying oxygen atmosphere (4-10% O₂/N₂), even though the raw data of the sensor response to this gas is rather small [4].

Fly ash particle samples with a known content of ammonia, originating from the urea/ammonia injection to remove nitric oxides in the catalytic converter of a power plant, were used as a demonstrator for the development of finger print detection of particles. The fly ash was heated and the emitted ammonia detected by a SiC-FET ammonia sensor as confirmed by an environmental mass spectrometer, see Fig. 2. Impedance spectroscopy of particles

adsorbed on IDEs has potential to detect concentration, size and eventually content of the particles. Resistivity measurements by IDEs may also reveal the concentration of particles.

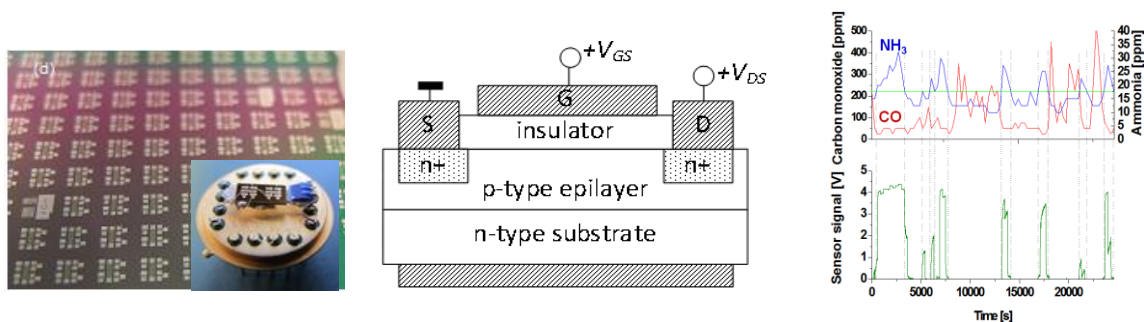


Figure 1. Left: SiC processed wafer with FET gas sensors. Insert: mounted sensor chip comprising two sensors. Middle: Schematic cross-sectional view of the gas sensitive SiC-FET. Right: Ammonia detection from a pre-set level of 15-20 ppm in varying environment up to 500ppm CO and 5% O₂/N₂.

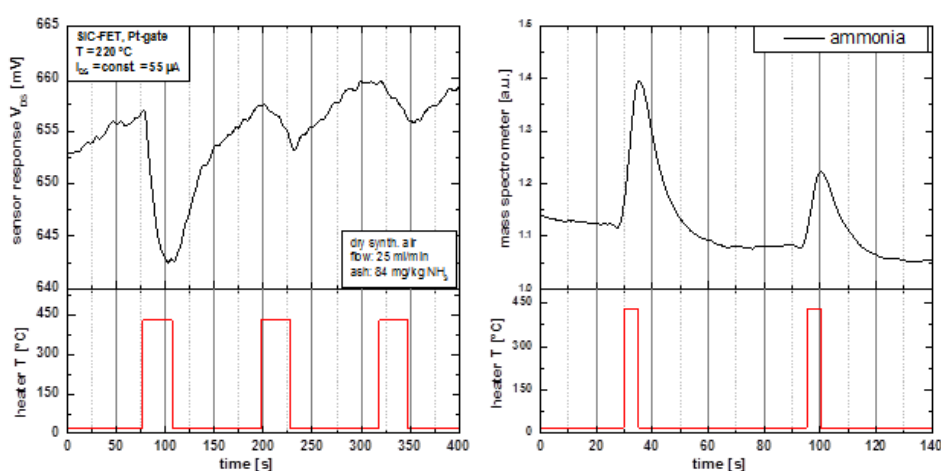


Figure 2. Left: Periodic heating of a fly ash sample and the sensor signal from a SiC-FET ammonia sensor. Right: Emitted ammonia at 430°C detected by an environmental mass spectrometer. (Signals smoothed by Savitzky-Golay Filter.) Copyright 2013 Society of Photo-Optical Instrumentation Engineers, SPIE [3]

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References

1. M. Andersson, R. Pearce and A. Lloyd Spetz, "New generation SiC based field effect transistor gas sensors," *Sens. Actuators B*, vol. 179, 2013 pp. 95 – 106.
2. C. Bur, P. Reimann, M. Andersson, A. Lloyd Spetz, and A. Schütze, "Increasing the selectivity of Pt-gate SiC field effect gas sensors by dynamic temperature modulation," *IEEE Sens. Journal*, vol. 12, no. 6, 2012, pp. 1906-1913.
3. A. Lloyd Spetz, Z. Darmastuti, C. Bur, J. Huotari, R. Bjorklund, N. Lindqvist, J. Lappalainen, H. Jantunen, A. Schütze and M. Andersson, Chemical sensor systems for environmental and emission control, *Proc. SPIE Defence, Security + Sensors*, Baltimore, USA, April 29-May 2, 2013.
4. Z. Darmastuti, C. Bur, P. Möller, N. Lindqvist, M. Andersson, A. Schütze, A. Lloyd Spetz, SiC-FET based SO₂ sensor for power plant emission applications, *Proc. Transducers 2013 & Eurosensors XXVII*, June 17-20, Barcelona, Spain, accepted.