Final Publishable JRP Summary for ENV01 MACPoll
Metrology for Chemical Pollutants in Air

Overview

This project set out to improve the metrological traceability and comparability of measurements produced by current air monitoring techniques and to provide the metrological and scientific tools to evaluate new sensor technologies used in air quality applications.
The project outcome has significantly contributed to fullfilling the data quality objectives of the European air quality regulation and it has provided key parts of the metrological backbone that will enable accurate and robust data of air pollution levels for the short and long term (trend) assessment.

Need for the project

The European Directive on “Ambient air quality and cleaner air for Europe” (2008/50/EC) sets limit values and data quality objectives (DQOs) for the measurement of air pollutants in ambient air in EU member states. Although a large number of documentary and physical standards are available, air monitoring networks are still struggling to comply with the quality objectives because of the lack of metrological transfer standards at and below the air pollutants limit values

The situation is even more critical in indoor air monitoring where no harmonised legislation is currently present and there is an urgent need for reference measurement methods and reference materials that help provide reliable data. Only recently, the European Construction Products Regulation (305/2011 EU) has introduced requirements on the emissions from construction products of dangerous substances, volatile organic compounds (VOC), greenhouse gases or dangerous particles into indoor or outdoor air.

Finally, the introduction on the market of small gas sensing devices seems to offer new perspectives for air monitoring because these devices are low-cost and provide real-time data. However, no thorough scientific and metrological evaluation of these new technologies has been performed to date.

This project addressed the need to improve the metrological traceability and comparability of measurements using current air monitoring techniques and the need to set-up a metrological basis for the new sensor technologies used in air quality applications.

These needs were demonstrated by:

- The poor agreement between reference standards prepared by NMIs for the calibration of air monitoring equipment;
- The lack of reliable “zero gas” for the zeroing of analysers and for the preparation of gas standards used in ambient air monitoring;
- The lack of accurate reference methods and traceable reference materials for the measurement of (semi)volatile organic compounds ((S)VOC) in indoor air;
- The lack of low-cost indicative measurement methods for Air Quality assessment that permit proper spatial coverage.

Scientific and technical objectives

One of the main objectives of the project was to comply with the challenging requirements of calibration gases, both for span (calibration point) and zero gas, as set out in documentary European standards related

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to the Air Quality Directive (2008/50/EC) reference methods. In order to achieve this, the project focussed on:

- Improvement of dynamic and static dilution, as alternative preparation methods to gravimetry, for the generation of reactive primary gas mixtures, namely nitrogen oxides (NO and NO_2) and sulphur dioxide (SO_2) at the limit values mandated by the Air Quality Directive
- Development of a new approach for single and simultaneous assessment of impurities in zero gas. Nitrogen and pure air, used for zeroing gas analysers and for dilution purposes, should be free of contaminants that may interfere with measurements

The second objective of the project was the development of references systems for (S)VOCs in indoor air pollution. To address this, the project aimed to:

- Improve reference methods and develop reference materials for harmful (S)VOCs originating from emission of building materials
- Develop a suitable reference material reproducing the gas emission behaviour typical of a construction product for the quality control of emission test chamber measurements

The third objective related to the applicability of micro-sensors in air quality monitoring. Micro-sensors are emerging measuring devices for the "indicative measurements" specified in the Air Quality Directive. The project therefore, focussed on:

- Setting up an evaluation protocol to evaluate the performance of micro-sensors for air monitoring and investigate the metrological aspects (traceability and uncertainty) of the results
- Developing a new highly sensitive and selective NO_2 sensor using the 2-D material graphene.

Results

Improvement of dynamic and static dilution, as alternative preparation methods to gravimetry, for the generation of reactive primary gas mixtures, namely nitrogen oxides (NO and NO_2) and sulphur dioxide (SO_2) at the limit values mandated by the Air Quality Directive

The project's evaluation of dynamic and static dilution preparation methods, for traceable calibration gases for SO_2, NO and NO_2 ambient air pollutants at concentrations close to the limit value, has led to the preparation of three guides for NMIs and air quality reference laboratories. The evaluation has also shown that the purity of the gases, including the dilution gas, is an important source of uncertainty.

To demonstrate the degree of comparability in measuring reactive air pollutants, two transfer standards, based on dilution techniques, have been designed, characterised and successfully used for the organisation of an interlaboratory comparison within the project partners. The Dynamic Dilution Standard (DDS) for the generation of NO and SO_2 pollutants close to the EU Air Quality Directive limit values was based on the dilution of a high concentrated gas standards with a Molbloc/Molbox mass flow system. The Traceable Mobile Permeation Generator (TMPG) for the NO_2 gas standards was based on a mass calibrated permeation unit and traceable gas flows and temperatures. The results of the comparison show that for NO and NO_2 it is in general possible to achieve a degree of comparability of 2-3 %, while for SO_2 the degree of comparability is approximately 5 %. This improved agreement for NO and NO_2 and the availability of transfer standards will help the comparability between air quality reference laboratories responsible for the quality assurance and quality control of the air monitoring networks in their country. In addition, air monitoring networks will be able to achieve the Air Quality Directive requirements (DQOs) for traceability and uncertainty for measurement at limit values and beyond.

Development of a new approach for single and simultaneous assessment of impurities in zero gas. Nitrogen and pure air, used for zeroing gas analysers and for dilution purposes, should be free of contaminants that may interfere with measurements

In this project particular emphasis was given to reactive contaminants in zero gas. Because zero gas (nitrogen or purified air) is used in analyser calibration, these impurities need to be minimised to (sub)-part per billion (ppb) levels and their presence quantified by traceable measurements using optical systems. In the case of the measurement of NO_2 impurities in zero gas, an innovative and sensitive cavity-enhanced detection system (CEAS) has been constructed based on a high-power blue light emitting diode. The performance of this CEAS system has been compared to a 'classical' chemiluminescence detector over the

trace level measurement range (ppb) with good results. However, in order to improve efficiency and reduce analysis costs, this project evaluated the feasibility of simultaneous detection of impurities. Due to species variability, two optical systems were developed; one system for hydrogen sulphide, water and carbon dioxide based on near-infrared spectroscopy, and one system for NO, NO_2, SO_2 and carbon monoxide based on mid-infrared spectroscopy.

An important issue in the development of analytical methods for measuring gases at trace levels is material compatibility. A comprehensive study of the adsorption of ammonia (reactive gas) at trace concentration levels (ppb) on different material surfaces (coated and non-coated stainless steel and various polymers) was carried out using a very sensitive cavity ring down spectrometer (CRDS) operating in the near infrared wavelength region. The overall adsorption on polymers was less than that on metal surfaces and results showed qualitative agreement with the obtained values in current literature. However, for some polymers showing low adsorption, our study revealed differences in adsorption which do not correspond with previous studies.

The research on zero gases was extended in the project, to the evaluation of systems for producing zero gas (purifiers and zero gas generators) and, based on this, to the preparation of a certification protocol for zero gas standards. The protocol produced describes the methodology that can be used to assign reference values, in amount-of-substance fractions, to the impurities in zero gas. In principle this document is for NMIs and calibration laboratories. However, laboratories operating in the field of gas analysis and in particular in ambient air measurements can also use it for the quality control of their zero gas.

Improve reference methods and develop reference materials for harmful (S)VOCs originating from emission of building materials

The research related to indoor air pollution focussed on a range of challenging (S)VOC that are typically emitted from building materials: hexadecane, dibutyl phthalate (DBP), dimethyl phthalate (DMP), 2-ethyl-1-hexanol, 1-methyl-2-pyrrolidone and styrene. The preparation of (S)VOC transfer standards at levels of interest for the emission testing laboratories was validated by the results of an interlaboratory comparison amongst the project partners. This study also highlighted the challenges in the standard preparation and the measurement of high boiling VOCs compounds due to their physical/chemical properties.

Develop a suitable reference material reproducing the gas emission behaviour typical of a construction product for the quality control of emission test chamber measurements

In addition, an innovative study on the production of a reference material for quality control of emission testing of VOCs less volatile than toluene was conducted. The study showed that a water-based clear lacquer spiked with VOCs was the most suitable support material. This lacquer was able to create a homogeneous surface after curing and to produce a high VOC release versus a low self-emission. This material has been already used as sample for an interlaboratory comparison for emission testing laboratories.

Setting up an evaluation protocol to evaluate the performance of micro-sensors for air monitoring and investigate the metrological aspects (traceability and uncertainty) of the results and

Developing a new highly sensitive and selective NO_2 sensor using the 2-D material graphene.

This project made an important step forward in the development, scientific validation and provision of metrological traceability of micro-sensors for air monitoring purposes. Two types of graphene sensors, based on epitaxial and exfoliated graphene, have been developed and their performance has been tested for the measurement of ambient levels of NO_2. The work on the optimisation of the sensor functionalization in order to improve the selectivity for NO_2 and on the annealing process has also led to promising results. In addition to this, a protocol for the evaluation of micro-sensors was developed and implemented in the assessment of the performances of gas sensors for NO_2 and ozone monitoring. The evaluation showed that the sensors are sensitive to the interference of other pollutants and to meteorological parameters such as temperature or humidity (depending on the measuring principle in use). It also showed that the model and calibration methodology that translate the sensor response in a measurement result are crucial for obtaining a reliable measuring device.

Finally, a clustered system, composed of different types of micro-sensors for the measurement of the air pollutants under the Air Quality Directive, was evaluated. The results showed that the use of an Artificial Neural Network using calibrated sensors achieved the best accuracy. However, when comparing the performance of the clustered system to the requirements (DQOs) for “indicative methods” of the Air Quality

Directive for different air pollutants, the clustered system was successful for ozone and, likely, for carbon monoxide only, but it was not satisfactory for nitrogen oxides. Furthermore, nothing could be concluded for sulphur dioxides because the levels of this pollutant in the air during the assessment were too low to be evaluated. The performance of the system towards carbon dioxide was also evaluated, although this is not a pollutant under the Air Quality Directive, and it showed that a very low uncertainty in the measurement of carbon dioxide ambient levels, down to about 3%, could be reached.

Actual and potential impact

The project's activities and results have been presented at international conferences, to specific ISO and CEN standardisation committees involved in air quality and gas analysis, and to stakeholders. The project has over 70 examples of dissemination including oral and poster presentations and 11 peer reviewed publications and a further six articles have been submitted for publication.

During the project, a stakeholder mid-term meeting, three workshops, respectively on zero gases, on ambient air and indoor air, and a final conference were organised between February 2013 and May 2014. All these events, which were targeted for an audience of 30-50 people, were well received and provided good opportunities for interactions between project collaborators, research organisations, air quality networks and industry.

The engagement opportunities with stakeholders also benefitted from the facts that project partners are members of key environmental networks, such as the AQUILA (Air Quality Reference Laboratories) European network, that they participate in standardisation activities (CEN/TC264 "Air Quality", CEN/TC 351 "Construction products: Assessment of release of dangerous substances" and ISO/TC158 "Gas Analysis") and that they provide traceable calibrations standards to air quality monitoring networks.

In particular the engagement with the AQUILA network helped the project partners to better understand measurement issues in the field. In return, the AQUILA network benefitted from the project's outputs on calibration gases, both for span and zero gas, as they will ensure the traceability and comparability of the measurement of chemical air pollutants in Europe and therefore the compliance with the data quality objectives of the Air Quality Directive.

Based on the outcome of the project's comparison on calibration gases for reactive pollutants, a new comparison is being organised within EURAMET to establish the comparability of SO_2 calibration gases at EU limit values. This comparison, open to European NMIs, will allow the scientific knowledge gained in the project to be used and shared within Europe.

Gas producers and manufacturers of purification systems and analytical equipment have given significant attention to the project's output on zero gas standards. The project's workshop on zero gases in June 2013, provided input to the publication of "Zero gas: Concept in search of a definition" written by L. Bergson, Tiger Optics (US) and published in Gases & Instrumentation. The protocol for certification of zero gas standards, developed by the project, has also been used for the certification of nitrogen and air zero gases prepared by a gas specialty producer. The intention was to feed the protocol into a new working item in preparation by ISO/TC158 committee. However, because of time constraints, it was agreed to wait for the revision of the documentary standard before including the project's input. Through this though, the documentary standard will offer a valuable and traceable methodology for NMIs and calibration laboratories but also, more in general, for the control of zero gases by end users.

The new reference materials and methods for indoor air produced by the project have been implemented by emission testing laboratories dealing with the emission of hazardous components from building materials. In particular, the reference material developed by the project to simulate the typical gas emission behaviour for a construction product has been used as sample specimen for an interlaboratory comparison to evaluate the quality of emission testing chambers of more than 50 laboratories. This output is therefore, contributing to compliance with the requirements of the new Construction Products Regulation and is a step towards reducing the risk of indoor pollution and health diseases caused by building materials.

The project's results on gas sensors for air monitoring have been recorded in a series of publicly available EUR publications. The "MACPoll protocol for the evaluation of sensors" (EUR report 26112) is currently used by the FP7 European project CITI-SENSE coordinated by the Norwegian Institute for Air Research (NILU). In addition, the results on the performance of a selection of micro-sensors for the measurement of specific air pollutants (NO_2 and ozone) are particularly beneficial for sensors manufacturers, and are helping them to build more reliable and accurate devices.

Air monitoring networks and environmental authorities have also benefitted from the project's outcomes on gas sensors, as they provide guidance on the state-of-the-art in gas sensing and help them to understanding the pros' and cons' of the sensor devices when applied in the field. In the near future, when gas sensor performances are successfully demonstrated, these devices could represent a new way to perform air monitoring, i.e. being used as indicative methods, allowed by the Air Quality Directive, with the advantages of being low-cost, providing real-time data and a large space coverage. Nitride Crystals Inc., USA and Perkin Elmer Inc., Canada have shown interest in testing and eventually producing the graphene sensors for NO_2 developed in this project.

List of publications

1 *Review of small commercial sensors for indicative monitoring of ambient gas*, M. Aleixandre, M. Gerboles, Chemical Engineering Transactions, 2012, Vol. 30, 169-174

2 *Precision quantum Hall resistance measurement on epitaxial graphene device in low magnetic field,* A. Satrapinski, S. Novikov, N. Lebedeva, Applied Physics Letters, 2013, Vol. 103, 173509

3 *Sensitivity optimization of Epitaxial Graphene Based Gas Sensors*, S.Novikov, A. Satrapinski, N. Lebedeva, I. Lisakka, IEEE Trans. On Instrum. and Meas., June 2013, Vol. 62, nr. 6, 1859-1864

4 *Adsorption of ammonia on treated stainless steel and polymer surfaces*, O. Vaittinen, M. Metsälä, S. Persijn, M. Vainio, L. Halonen, Applied Physics B: Lasers and Optics, May 2014, Vol. 115, Issue 2, 185-196

5 *Development of a material with reproducible emission of selected volatile organic compounds - µ-Chamber study*, M. Nohr, W. Horn, K. Wiegner, M.Richter, W. Lorenz, Chemosphere, July 2014, Vol. 107, 224–229

6 *Optimization of Epitaxial Graphene Based Gas Sensors*, S. Novikov, A. Satrapinski, N. Lebedeva, I. Lisakka, Digest on CPEM 2012, 2-5 July 2012, Washington, pp. 602-603

7 *Ultra-sensitive nitrogen dioxide sensor based on graphene*, S. Novikov, N. Lebedeva, A. Satrapinski, Nordic semiconductor meeting (http://physics.aalto.fi/~filip/abstracts/32_Novikov_poster.pdf)

8 *Characterization of epitaxial and CDD graphene with double metal-graphene contacts for gas sensing*, S. Novikov, J. Hämäläinen, J. Walden, I. Lisakka, N. Lebedeva, A. Satrapinski, 16th International Congress of Metrology (DOI:10.1051/Metrology/2013113003)

9 *Calibration gases for existing Air Quality Directive pollutants at limit values (LV)*, T. Macé, J. Couette, F. Dijoux, F. Mary, C. Sutour, B. Niederhauser,H.P. Haerri, C. Pascale, J. Walden, K. Wirtz,V. Stovcik, 16th International Congress of Metrology (DOI:10.1051/Metrology/201310004)

10 *European project: Metrology for Chemical Pollutants in Air,* A. Baldan, 16th International Congress of Metrology (DOI:10.1051/Metrology/201310002)

11 *Calibration of Small Resistive Commercial Sensors to Measure Ozone with the Interference of Temperature and Humidity*, M. Aleixandre, M. Horrillo, M. Gerboles, L. Spinelle, Sensors, 2013 IEEE (DOI:10.1109/ICSENS.2013.6688514, 2013, Page(s): 1 – 4)

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