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JRP-Coordinator	
Name, title, organisation	Mrs. Annarita Baldan, VSL B.V.
Tel:	+31 15 2691728
Email:	ABaldan@vsl.nl
JRP website address	www.macpoll.eu
Other JRP-Partners	
Short name, country	
	VSL, The Netherlands
	BAM, Germany
	IL, Finland
	INRIM, Italy
	JRC, European Commission
	LNE, France
	METAS, Switzerland
	MIKES, Finland
	NPL, United Kingdom
	PTB, Germany
	SMU, Slovak Republic
	UBA, Germany

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REG1-Researcher
(associated Home Organisation)

Researcher name, title	Dr. Manuel Aleixandre	Start date: 1 August 2011
(Home organisation Short name, country)	CSIC, Spain	Duration: 34 months (50 %)

REG2-Researcher
(associated Home Organisation)

Researcher name, title	Dr. Olavi Vaittinen	Start date: 1 August 2011
(Home organisation Short name, country)	UH, Finland	Duration: 18 months

REG3-Researcher
(associated Home Organisation)

Researcher name, title	Dr. Serguei Novikov	Start date:1 Oct 2012
(Home organisation Short name, country)	Aalto, Finland	Duration: 18 months

RMG1-Researcher
(associated Empl. Organisation)

Researcher name, title	Dr. Tanil Tarhan	Start date:1 Nov 2012
(Empl. organisation Short name, country)	TUBITAK, Turkey	Duration: 6 months

ESRMG1-Researcher
(associated Empl. Organisation)

Researcher name, title	Mr. Nikola Škundrić	Start date:1 May 2013
(Empl. organisation Short name, country)	DMDM, Serbia	Duration: 3 months

TABLE OF CONTENTS

1   Executive Summary

Introduction

The MACPoll project has significantly contributed to fullfilling the data quality objectives of the European air quality regulation. It has done this by providing key parts of the metrological backbone that will enable accurate and robust data of air pollution levels for the short and long (trend) term assessment.

The Problem

The European Directive on "Ambient air quality and cleaner air for Europe" (2008/50/EC) sets limit values and data quality objectives 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.

The situation is even more critical in indoor air monitoring where no harmonised legislation is currently available and there is an urgent need for reference measurement methods and reference materials to help provide reliable data.

Finally, the introduction into the market of small gas sensing devices could offer new perspectives for air monitoring as these devices are low-cost and provide real-time data. However, no thorough scientific and metrological evaluation of these new technologies has been performed so far.

The Solution

This project set out to improve the metrological traceability and comparability of measurements using current air monitoring techniques and to provide the metrological and scientific tools to evaluate new sensor technologies used in air quality applications. To achieve these goals, the project focussed on:

Improving the agreement between reference standards prepared by NMIs for the calibration of ambient air monitoring equipment;

Developing a certification protocol for zero gas standards used for the zeroing of analysers and dilution of concentrated gas standards;

Producing accurate reference methods, traceable reference materials and constant emitting materials for the measurement of (semi)volatile organic compounds ((S)VOC) in indoor air;

Developing new micro-sensors based on graphene. As well as preparing an evaluation protocol for micro-sensors and assessing their performance for the measurement of specific air pollutants.

Impact

The outputs from the project, such as the improved reference standards for ambient air monitoring and the new reference materials and methods for indoor air have already been implemented by the EU air quality networks and by the emission testing laboratories (respectively) dealing with the emission of hazardous components from building materials. Through this, the air quality measuring community has taken a positive step towards compliance with the requirements of both the EU Air Quality Directive and the new Construction Products Regulation (305/2011 EU).

In the longer term, it is expected that the certification protocol for zero gases and the evaluation protocol for micro-sensors (developed by the project) will feed into the preparation or revision of documentary standards in European and International technical committees dealing with gas analysis and air quality.

The project's outputs relating to micro-sensors for air monitoring have so far had the largest impact as they have helped sensors manufacturers to build reliable and accurate devices. In addition, they have helped decision makers evaluate the benefits and limitations of these sensor devices when applied in the field. In the longer term, this will impact the implementation of the EU Air Quality Directive (2008/50/EC) and in particular on the use of indicative methods for ambient air monitoring.

2   Project context, rationale and objectives

2.1   Context

The measurement of gaseous pollutants in air is a sensitive and important issue as it has a large impact on human health and the environment.

The European Directive on "Ambient air quality and cleaner air for Europe" (2008/50/EC) sets limit values to the concentration levels of primary gas pollutants (i.e. sulphur dioxides, nitrogen oxides, carbon monoxides, benzene and ozone) and data quality objectives for their measurement in the EU member states. As well as ensuring metrological traceability, the data quality objectives also specify the maximum allowable uncertainty for fixed and indicative measurement data.

Each European country currently has a network of monitoring stations that measure ambient air pollutants and report the results back to AirBase; the public database of the European Environmental Agency. In addition, the European Air Quality Reference laboratories (AQUILA) network ensures the implementation of the Air Quality Directive and the harmonisation and comparability of the thousands of measurements taken throughout Europe.

Although no harmonised legislation is currently in place for the monitoring of indoor air, concern regarding the exposure to indoor chemical pollutants is significantly increasing. Banning strategies have already been applied in the last decade, such as banning smoking in indoor public places or banning the use of formaldehyde in certain applications. Recently, the European Construction Products Regulation (305/2011 EU) has also 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. The harmonisation of test methods and of labelling of products, stimulated by this regulation, contributes to the reduced trade barriers for construction products in the European market.

The future of air quality assessment will rely on more spatial and exposure based monitoring of air pollutants (indicative measurements). In addition, the need for mobile applications and better spatial coverage can only be satisfied by reducing the size and costs of monitoring devices using for example micro-sensors. Currently, a variety of micro-sensors (solid state, electrochemical, fibre optical, etc.) have been introduced into the market but their suitability for air monitoring still needs to be assessed.

2.2   Rationale

In support of the enforcement of the Air Quality Directive and of the Construction Products Regulation, standardisation and metrological activities are deemed of fundamental importance as together they provide a proper measurement infrastructure.

Although NMIs have been providing, for a long time, calibration gases to air monitoring networks for the calibration of their equipment, the results of key-comparisons (comparison exercises amongst NMIs to establish the degree of comparability of the national standards) show that the comparability of these calibration gases is not satisfactory.

In addition, there is a lack of stable Certified Reference Materials (CRM) in cylinders for reactive gases, more specifically nitrogen oxides (NOx) and sulphur dioxide (SO$_2$) at the limit values (parts per billion levels) mandated by the Air Quality Directive. This situation limits the possibility of offering traceable gas mixtures for the calibration of analysers in air quality measurements and in particular for those located in rural or remote areas where the concentration of pollutants is low. Alternative traceable methods for the preparation of standard gas mixtures, such as dynamic and static dilution techniques, can be used, however their performance and comparability needs to be investigated.

The quality of the zero gas (nitrogen and clean air), used for the zeroing of analysers and as dilution gas in the preparation of gas standards, has a significant role in air monitoring where trace concentration levels are measured. The zero gas should be free of contaminants that may interfere with the measurements. However, currently zero gas does not fulfil the quality specifications stated in the European documentary standards related to air monitoring reference methods and it lacks metrological traceability. The certification of the (im)purity composition of zero gas is also not a capability within the remit of most EU air quality monitoring networks and instead it should be provided by NMIs.

In indoor air measurements, major hazardous pollutants originating from emission of building materials are volatile organic compounds (VOCs). At present, more than 15 documentary standards, most of them under

the ISO 16000 series, have been developed or are in preparation to cope with the need to measure different VOCs gaseous species respective of their application and concentration levels. But in order to support their implementation, metrology, in the form of reference materials and methods, is needed to provide traceability and ensure harmonisation (Quality Assurance and Quality Control (QA/QC)) of measurements in the field. In particular, the group of semi- volatile organic compounds ((S)VOCs) need calibration standards and reference materials. ((S)VOCs), such as phthalates, are VOCs with high boiling points (above 250 °C) and are listed in the "Candidate List of Substances of Very High Concern for authorisation" prepared by the European Chemicals Agency (ECHA) as a follow on from the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) directive.

Further to this, the release to market of "novel" sensor-based micro-devices suitable for air monitoring has raised public and the decision makers' attention. These low-cost systems could potentially be used as indicative methods allowed by the Air Quality Directive with the advantage of providing real-time data and large spatial coverage. However, the validation of the micro-sensors carried out so far, has lacked a structured and metrological approach, and further research is needed for more sensitive sensors able to discriminate chemical pollutants at very low concentration levels.

2.3 Objectives

This project aimed to improve the metrological traceability and comparability of measurements in current air monitoring techniques and to set-up the metrological basis for the use of new sensor technology in air quality applications.

One of the main objectives of this project was to support compliance with the requirements of calibration gases, both span (calibration point) and for zero gas, as stated in European documentary standards related to the Air Quality Directive (2008/50/EC) reference methods. To achieve this, the project focussed on:

- The improvement of dynamic and static dilution preparation methods for calibration gases for NOx and SO2 at the EU Air Quality Directive limit values. In order to reduce their uncertainty, demonstrate their comparability and suitability for implementation at air monitoring networks.

- The development of optical traceable analytical methods, such as Cavity Ring Down Spectroscopy (CRDS) or Tunable Diode Laser Absorption Spectroscopy (TDLAS) for the (simultaneous) assessment of trace impurities in zero gases and in particular for those impurities interfering with the measurement of reactive gases. Part of the analytical method development is the study of material compatibility especially for ammonia that easily adsorbs and reacts on contact surfaces.

The second objective for the project was based on the needs in indoor air pollution and in particular on the metrological gaps identified by emission testing laboratories for the implementation of the Construction Products Regulation. To address this objective the project focussed on the preparation of gas standards and reference materials for the measurement of VOC and (S)VOCs. In particular the:

- Development of reference systems (gas standards and measurement methods) for a selection of VOCs and (S)VOCs measured in indoor air monitoring.

- Preparation of a constant emitting reference material for the quality control of emission test chamber measurements.

The last objective of the MACPoll project addressed the issues surrounding micro-sensors and their applicability in air quality monitoring. For this the project focussed on:

- Development of an evaluation protocol to verify the performance of micro-sensors as an "indicative method" according to the Air Quality Directive and of QA/QC procedures for the calibration of sensors. The project also focussed on the assessment of the performance of a selection of micro-sensors for the measurement of specific air pollutants.

- Development of a new highly sensitive and selective NO2 sensor using the 2-D material graphene.

3   Research results

3.1   The improvement of dynamic and static dilution preparation methods for calibration gases for NOx and SO2 at the EU Air Quality Directive limit values. In order to reduce their uncertainty, demonstrate their comparability and suitability for implementation at air monitoring networks.

3.1.1   Revised methods for generating calibration standards for SO_2, NO, NO_2 at limit values

This consisted of revising the primary methods for the preparation of calibration gas standards for challenging pollutants with traceability to SI units and targeting the relative uncertainties to a maximum of 3 %. The research focused on the reactive pollutants SO_2, NO and NO_2 and covered the ranges of hourly and annual limit values given in the European Directive on "Ambient air quality and cleaner air for Europe" (2008/50/EC). According to the data quality objectives of this directive, the maximum allowed uncertainty for fixed measurements of these components in ambient air is 15 %.

For NO, the selected dilution methods were the static volumetric dilution and the dynamic dilution of concentrated gas mixtures (Certified Reference Materials, CRM's prepared by gravimetric method). The concentration range investigated was between 20 and 100 nmol/mol (ppb).

The revisited dilution methods for NO_2, were the permeation method, the dynamic dilution of concentrated gas mixtures and the gas phase titration method. The concentration range investigated was between 20 and 80 nmol/mol (ppb).

For SO_2, the selected dilution methods were the static dilution method, the permeation method and the dynamic dilution of gas mixtures. The concentration range investigated was between 40 and 150 nmol/mol (ppb).

After thorough revision and improvement of their preparation methods, LNE, METAS, IL, UBA and SMU shared their expertise and findings and produced three guides on the generation of standard gas mixtures for reactive pollutants at the EU directive limit values:
1   Guide on dynamic dilution methods for NO, NO_2 and SO_2 at limit values;
2   Guide on permeation method for the dynamic generation of NO_2 and SO_2 standard gas mixtures at limit values;
3   Guide on static dilution method for NO, NO_2 and SO_2 at limit values.

3.1.2   Harmonisation of the revised methods by comparison using travelling standards

An interlaboratory comparison was organised to evaluate the comparability between the revised calibration gas preparation methods developed. The comparison aimed to evaluate the suitability of the static dilution method for SO_2 and NO, the permeation method for NO2 and SO2 and the dynamic dilution method for NO, NO_2 and SO_2. LNE was coordinator of the interlaboratory comparison. METAS, IL, UBA and SMU were the other participants.

In contrast to the normal procedure for comparisons in gas analysis, the travelling standards used were not gas mixtures stored in vessels, but "travelling" traceable gas generation systems based on dilution technologies. Two travelling standards were designed, characterised and circulated amongst the participating laboratories:

1   For NO and SO_2, a Dynamic Dilution Standard (DDS) was developed by LNE. It was composed of a Molbloc/Molbox mass flow system;

2   For NO_2, a Traceable Mobile Permeation Generator (TMPG) was developed by METAS. It uses a mass calibrated permeation unit and traceable gas flows and temperatures.

The principle of the DDS is to dilute gas mixtures containing large amounts of substance in fractions with zero air in order to dynamically generate gas mixtures with 20 and 100 nmol/mol for NO and 40 and 150 nmol/mol for SO_2, respectively. The DDS developed by LNE is shown in *Figure 1*. It is composed of two Molbox1 mass flow terminals operating in conjunction with two Molbloc laminar mass flow elements. These elements are connected in parallel and supplied respectively with the large amount of substance in fractions of gas mixture and the dilution gas (synthetic air).

The system of Molbox/Molblocs allows a nominal mass flow range between 0.1 mg/s and 1 mg/s (5 ml/min to 50 ml/min for nitrogen) for the concentrated gas mixture flow and a range between 10 mg/s and 100 mg/s (0.5 l/min to 5 l/min for air) for the dilution gas flow, respectively. All flow meters were calibrated by the gravimetric dynamic method and have expanded uncertainties below 0.3 %.

In order to obtain the targeted amount of substance in fractions of the gas mixtures, the mass flow of each gas line was set and maintained by a thermal mass flow controller (MFC) with control software (MFC from AERA manufacturer). In conjunction with downstream pressure regulators, this system controls the delivered mass flow for obtaining gas mixtures with a constant amount of substance. A mixing chamber at the exit of the DDS ensured the homogeneity of the dynamic gas mixtures an all relevant data was recorded with a laptop computer.

Figure 1: Representation of the Dynamic Dilution Standard (DDS)

The principle of the TMPG developed by METAS for generating NO_2 calibration gas mixtures was based on the permeation method. The system is shown in *Figure 2*. It is composed of an oven with an SI-traceable temperature sensor, gas flow controllers, a meter and a pressure controller. The NO_2 is released by a mass calibrated permeation device whose permeation rate has been previously calibrated in a magnetic suspension balance, according to ISO 6145-10. For controlling and measuring the carrier and dilution gas flows, two MFCs and a mass flow meter (MFM) were used. With the 0.5 slm MFC a constant gas flow of 0.3 L/min was maintained through the oven. In contrast the dilution flow is adjustable between 0.5 to 5 L/min with a 5 slm MFC, depending on the set amount of substance fraction. A 6 slm MFM measured the actual total carrier and dilution gas flows.

Figure 2: Representation of Traceable Mobile Permeation Generator (TMPG)

The characterisation of the two dynamic dilution systems demonstrated that they were accurate, stable and reproducible standards for generating calibration gas mixtures even when travelling to the field.

The two travelling standards were circulated among the participating laboratories during the interlaboratory comparison in 2013 according to the schedule given in *Figure 3*.
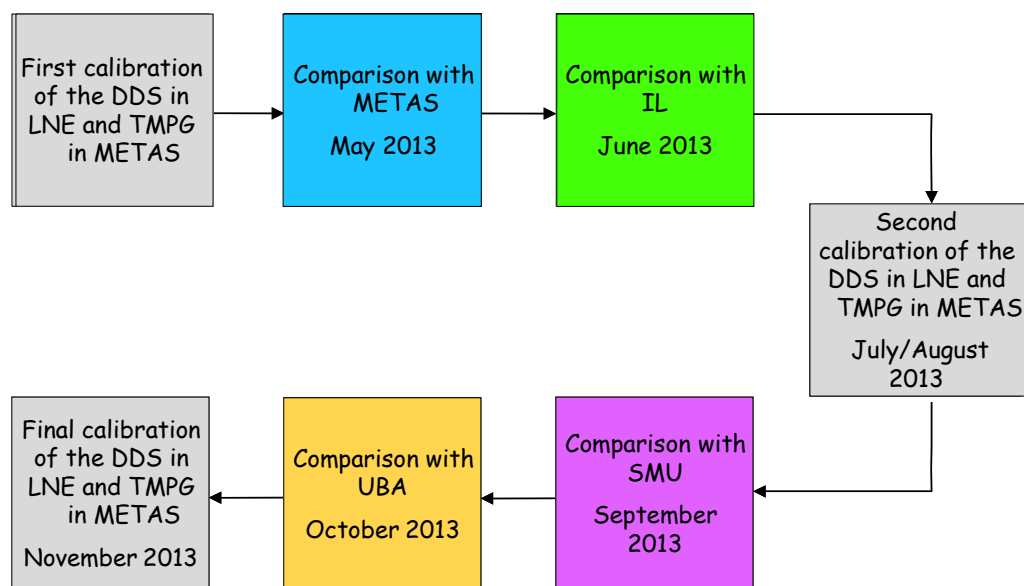
Figure 3: *Schedule for the comparison amongst participating laboratories. METAS (Switzerland), IL (Finland), LNE (France), SMU (Slovakia), UBA (Germany)*

In order to demonstrate that the requirements of the European Directive on "Ambient air quality and cleaner air for Europe" (2008/50/EC) could be met, dynamic gas mixtures were generated with the travelling standards, at amounts of substance in fractions corresponding to the limit values given in the European Directive. The DDS was used for the generation of dynamic gas mixtures with two stable low concentrations in matrix "air" at 40 and 150 nmol/mol for SO_2 and at 20 and 100 nmol/mol for NO. The TMPG was used for the generation of NO_2 dynamic gas mixtures at 20 and 80 nmol/mol.

After each participant had calibrated their analysers with their own standard, dynamic gas mixtures of NO, NO_2 and SO_2 generated with the two travelling standards were measured according to the revised methods.

An initial target was set for the degree of comparability between the measurement results and the reference values provided by the travelling standards: this was better than ± 2 % for NO at 20 and 100 nmol/mol, better than ± 2 % for SO_2 at 40 and 150 nmol/mol and better than ± 3 % for NO_2 at 20 and 80 nmol/mol.

The results of the interlaboratory comparison showed that for NO at 20 and 100 nmol/mol the degrees of equivalence fulfilled the requirement of 2 %, except for two laboratories (IL, SMU) at 20 nmol/mol.

For SO_2 at 40 and 150 nmol/mol the degrees of equivalence were approx. 5 % and therefore the target of 2 % could not be met, with exception of LNE. Positive deviations between the amount of substance in the fractions measured by the participants and the reference value (DDS) was also observed.

Regarding NO_2 at 20 and 80 nmol/mol the degrees of equivalence met the target agreement of 3 % for almost all the participants with the exception of UBA at 20 and 80 nmol/mol and METAS at 20 nmol/mol.

The interlaboratory comparison also showed that for some laboratories the expanded uncertainties for the measurement results were high (11 % for NO and NO_2 at 20 nmol/mol for UBA and 8% for SMU for NO at 20 nmol/mol). These laboratories will therefore have to modify their calibration methods in order to decrease their uncertainties and improve the accuracy of their measurement results.

Conclusions

This work has led to the improvement of dynamic and static dilution preparation methods for calibration gases for NOx and SO_2 at the EU Air Quality Directive limit values. This has reduced the uncertainty and demonstrated their comparability and suitability for implementation by air monitoring networks.

The three guides produced on the generation of standard gas mixtures for reactive pollutants at the EU directive limit values, provide guidance on how to generate SO_2, NO and NO_2 standard gas mixtures in relevant concentration ranges and with associated uncertainties in accordance with the specifications given

in the European Directive 2008/50/EC and associated EN standards. The target users for the guides are the NMIs and the European Reference Air Quality laboratories responsible for providing traceability, calibration and quality control to air monitoring networks.

In addition, the interlaboratory comparison on the comparability between the revised calibration gas preparation methods developed was a good opportunity to exchange technical knowledge amongst the participants and to share their experience in the generation of standard gas mixtures. With exception of SO_2 the results of the interlaboratory comparison met the target objectives, regarding the suitability of the static dilution method for SO_2 and NO, the permeation method for NO_2 and SO_2 and the dynamic dilution method for NO, NO_2 and SO_2. A new comparison for SO_2, outside the activities of this project, will be organised within EURAMET.

3.2   The development of optical traceable analytical methods, such as Cavity Ring Down Spectroscopy (CRDS) or Tunable Diode Laser Absorption Spectroscopy (TDLAS) for the (simultaneous) assessment of trace impurities in zero gases and in particular for those impurities interfering with the measurement of reactive gases. Part of the analytical method development is the study of material compatibility especially for ammonia that easily adsorb and reacts on contact surfaces.

3.2.1   Case Study: adsorption measurements of ammonia on metal and polymer sample lines

Ammonia (NH_3) is a reactive gaseous pollutant that contributes to acid deposition, eutrophication and secondary particulate aerosol formation. Typical atmospheric fractions of NH_3 are at the lower nmol/mol level but in heavily contaminated areas this may rise to µmol/mol levels. Several studies have shown that reliable measurement of low amount fractions of NH_3 is highly challenging due to NH_3's high water solubility and polarity. Therefore, reliable measurement data cannot be obtained if water condensation and adsorption/desorption effects occurring on the surfaces of the sampling system and measuring equipment are not taken into account.

REG(UH) developed a measuring set-up to quantify the NH_3 adsorption using a cavity ring down spectrometer (CRDS) operating in the near infrared wavelength region. A protocol was prepared for measurements to evaluate the adsorption effect of NH3 using several different materials:

- metals such as (electro-polished) stainless steel 316L
- silicon-coated surfaces (SicoNert 1000, SilcoNert 2000 and Dursan)
- polymers including PTFE, PVDF, FEP

A typical measurement result is shown in *Figure 4*. As can be seen, first the gas flow containing a low concentration fraction of NH_3 is directed via the bypass. Then a rapid switch is made to the test tube which leads to a sharp decrease in the measured amount fraction. Finally a slow recovery of the NH3 amount fraction is observed.
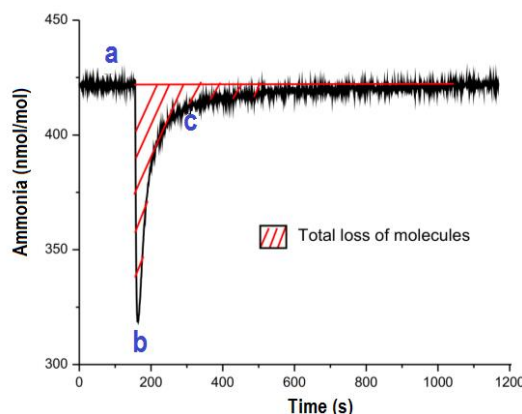

Figure 4: *Example of the NH3 time evolution in an adsorption experiment. a): NH3 gas flow goes via the bypass. b) Switch to the test tube leads to a sharp decrease in the measured amount fraction c) Slow recovery of the NH3 gas phase concentration.*

The measurements were predominantly found to be reproducible within 20 %, although the overall adsorption on polymers was less than that on metal surfaces. Results showed in general qualitative agreement with the obtained values in literature. However, for some polymers showing low adsorption the results revealed differences in adsorption which were no comparable to previous studies. The results were also compared to those obtained by cavity enhanced absorption spectroscopy at VSL and they agreed with the uncertainty levels for the studied surfaces.

3.2.2   Simultaneous detection of zero gas impurities at specification levels

Quantifying different impurities in zero gas necessitates the use of several dedicated analytical instruments. For each measurement the instrument and sampling system must be equilibrated and for reactive gases at

nmol/mol levels this equilibrium state can take up to several hours, meaning that these measurements are both expensive and time-consuming.

In order to improve efficiency and to reduce the costs of analysis of zero gas, analytical methods, suitable to detect a larger group of compounds, were developed. The zero gas impurity concentration levels under investigation in the MACPoll project were those specified in the EN documentary standards relative to the reference methods for the measurement of the concentration of NO_2 and SO_2 (EN14211, EN14212). Due to species variability, two systems were developed in the project:

1   H_2S, H_2O, and CO_2 were measured with a near-infrared spectroscopic technique and

2   NO, NO_2, SO_2 and CO were measured with a mid-infrared spectroscopic technique.

Near-infrared spectroscopic technique

The near-infrared system was a combination of a direct absorption based instrument developed by PTB for the measurement of H_2O and CO_2 and a modified, commercial CRDS spectrometer for the measurement of H_2S property of MIKES. Prior to the measurements certain parameters were characterised including:

- Laser characterisation: Wavelength and light power of the laser were analysed. An appropriate modulation scheme was implemented in order to assess the spectral lines of interest as well as to have a sufficiently large spectral window for baseline fitting on the recorded scans.

- Spectral line parameters: Line strengths of two lines in the v1+v3 CO_2 band were recorded and later used for amount fraction measurements in zero gas. The derived line strengths were $1.593 \cdot 10^{-20}$ cm/molecule for the P36e line and $1.981 \cdot 10^{-20}$ cm/molecule for the P34e line, with relative expanded uncertainties of 1.1 % and 1.3 %. These values agreed well with data listed in the HITRAN2008 database, and possess at least a factor of two lower uncertainties. Uncertainties were calculated according to the GUM and partially achieved traceability of the line strength results. Line strengths of water vapor were taken from the HITRAN 2008 database.

- Optical path length calibration: Laser distance meters were used for the traceable determination of the optical path length of the gas cell. The obtained path length was 76.643 m with an expanded uncertainty of 0.032 m.

Typical measured spectra are shown in *Figure 5*. The results of these measurements show that the spectrometer is suitable for simultaneous measurement of the two analytes at the limit amount of fraction levels for zero gas. A relative expanded uncertainty was obtained for CO_2 of 2.4 % (limited by the uncertainty of the fit area) and for H_2O of 11 % (limited by the 10 % uncertainty of the line strength in the HITRAN database).
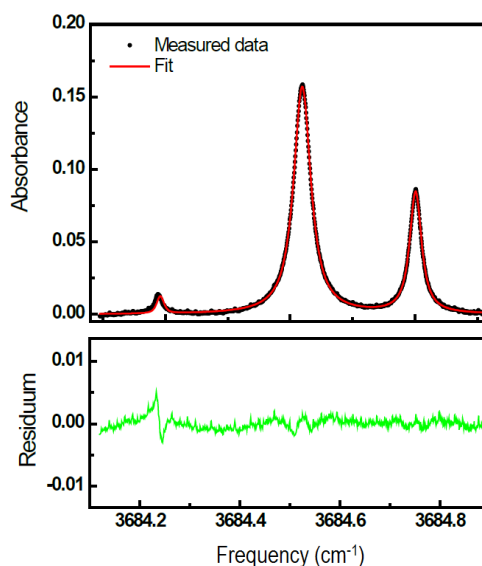
Figure 5: Measured spectrum of 4 µmol/mol CO_2 and 90 µmol/mol H_2O and the fit residual.

System integration of the H_2S CRDS system and the H_2O and CO_2 direct absorption system was realised by combining the gas handling and the data acquisition system of the two spectrometers. This was done during a joint measurement campaign by MKES and PTB. During this week long campaign, simultaneous detection of the three analytes was produced.

Mid-infrared spectroscopic technique

The mid-infrared spectroscopic system was a compact, commercial Quantum-Cascade laser absorption spectrometer used for the analysis of four compounds (NO, NO_2, SO_2 and CO) at low mol fractions. The system incorporated four pulsed QC lasers and a 210 m path length absorption cell to obtain very long path lengths in a small volume. An analysis flow rate of 1 L/min was required to prevent adsorption phenomena and detection limits were 0.5 nmol/mol for all compounds. An uncertainty budget was set up taking into account such factors as pressure, temperature, cell length, line strength, and line area of the fit. The latter two factors were found to be the dominant ones.

3.2.3   Certification protocol for assigning values to zero gas

A protocol for the certification of zero gas standards was developed based on the previous work and in addition on:

Development of a measurement approach for the detection of SO_2, NO and NO_2 zero gas impurities

Conventional trace analysers based on chemiluminescence (NO and NO_2) and fluorescence (SO_2) were used to perform measurements at (sub) nmol/mol levels. The measurement uncertainty was calculated and detection limits were determined using the standard addition method. This method consisted of a dynamic spiking of zero gas with known and traceable amounts of the impurity. For NO and NO_2 detection limits down to 0.08 nmol/mol (SNR=3) were established.

Parallel to this, optical systems based on spectroscopic techniques were tested. LNE used a commercial spectrometer based on direct absorption measurements using Quantum Cascade Lasers for SO_2, NO, NO_2 detection. VSL developed a cavity-enhanced spectrometer (CEAS) based on a blue LED for NO_2 detection. As a the final step, for SO_2 and NO_2, a successful cross-check of the results was obtained by applying and comparing spectroscopic and conventional techniques.

Develop traceable standards for zero gas

Preparation methods for zero gas for actual ambient air measurements of SO_2, NO, NO_2 and CO were developed. For this, 2 different gas purifiers and 3 zero air generators were tested by LNE, NPL and VSL.

The purifiers removed SO_2, NO and NO_2 from air and nitrogen to a level below 1 nmol/mol at the point of use. CO was only removed by one purifier to this level whilst the other purifier did not remove CO at all. Tests of the zero air generators revealed that NO and NO_2 output levels of the generators were in line with the specification set for zero gas in the EN14211 (≤1 nmol/mol).

Workshop on zero gases

In June 2013 the project organised and held a workshop on zero gas for participants from standardisation organisations, industry and research organisations. A guide to the certification protocol for zero gases was presented (in part based on a questionnaire sent out to stakeholders) and resolutions were adopted on different aspects of zero gas standards.

The developed certification protocol presented several techniques that can be used to assign reference values, in amount-of-substance fractions, to the impurities in zero gas. The protocol also provided guidance on how to use relative methods and absolute methods in assigning values.

The certification protocol provides guidance on the certification or verification of impurities that can influence the quality of compressed zero gas in cylinders, the quality of purification systems and zero gas generators. In principle the document is meant 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.

Conclusions

This work led to the development of optical traceable analytical methods, such as Cavity Ring Down Spectroscopy (CRDS) or Tunable Diode Laser Absorption Spectroscopy (TDLAS) for the (simultaneous) assessment of trace impurities in zero gases and in particular for those impurities interfering with the measurement of reactive gases. Part of the analytical method development was the study of material compatibility especially for ammonia that easily adsorbs and reacts on contact surfaces. All activities related to the assessment of zero gas were completed as proposed. In addition, the collaboration of external parties, manufacturers of purification systems and of zero gas generation systems was essential for completing this part of the project successfully.

Key outputs of this part of research, besides the successful assessment of trace levels of contaminants in zero gases, are the fabrication of a prototype CEAS (Cavity Enhanced Absorption Spectroscopy) based on a blue led light for the assessment of NO_2 and the preparation of the certification protocol for zero gases.

The CEAS is a unique equipment because, in contrast to the widely used chemiluminiscence technique, it is selective for NO_2 and less expensive. The first validation of the CEAS in the laboratory has shown promising results, but further validation is needed.

The certification protocol for zero gas standards prepared at the end of the research activities is an important step for improving the accuracy of air monitoring and of industrial applications especially when the component concentration levels are low like in the semicon sector. This protocol now needs to be implemented by gas manufacturers to guarantee the quality of the zero gas they produce as well as by end users to be able to verify their analytical equipment.

3.3   Development of reference systems (gas standards and measurement methods) for a selection of VOCs and (S)VOCs measured in indoor air monitoring

Volatile organic compounds (VOCs) found indoors have the potential to affect human health. Typical sources include building materials, furnishings, cleaning agents, etc. To address this risk, chemical emission testing is used to assess the potential of different materials to pollute indoor air. To do this, the material under investigation is placed in an emission test chamber and the concentration of the emitted gas monitored over time (See Figure 6).
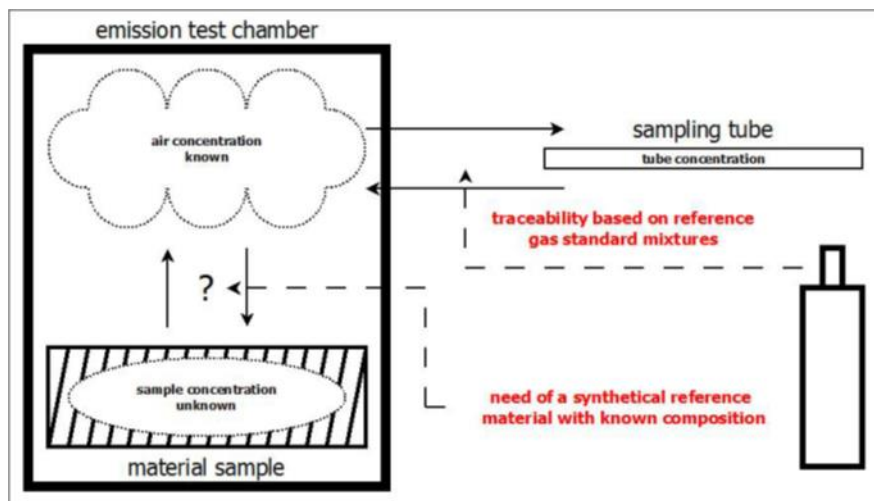

Figure 6: Measurement procedure in emission testing

However, in order to obtain reliable measurement results, both the measurement data and the emission test system need to undergo a thorough QA/QC process. This project aimed to provide metrological solutions to emission testing of VOCs and (S)VOCs by developing gas standards and reference materials. The research focussed on the generation of accurate reference gas mixtures (standard atmospheres) for a selection of (S)VOCs and on the development of a solid reference material with a compound release behaviour typical of a test specimen. This material should be suitable for comparison of measurement results between test laboratories and as for the quality control of the test procedure for a laboratory's testing chamber. The use of reference materials is recommended by the technical specification CEN/TS 165161, developed by CEN/TC 351/WG 2 "Emissions from construction products into indoor air" for the enforcement of the European Construction Products Regulation (CPR).

The VOCs and (S)VOCs selected for the study, were compounds typically found in indoor air and were relevant to the "Candidate List of Substances of Very High Concern for authorisation" prepared by the ECHA as a follow on from the REACH directive. The compounds of interest are listed in Table 1.

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[1] CEN/TS 16516:2013. Construction Products – Assessment of release of dangerous substances – determination of emissions into indoor air

Table 1: List of compounds

Compound	Formula	Bp. [°C]	Justification
n-hexadecane	$C_{16}H_{34}$	287	▪ part of many building products, e.g. paints, flooring material ▪ often measurable in a big group of similar compounds
dibutyl phthalate (DBP)	$C_{16}H_{22}O_4$	340	▪ plasticiser ▪ on ECHA list
dimethyl phthalate (DMP)	$C_{10}H_{10}O_4$	282	▪ plasticiser
2-ethyl-1-hexanol	$C_8H_{18}O$	182	▪ emits from carpets, flooring materials PVC-type
1-methyl-2-pyrrolidone (NMP)	C_5H_9NO	203	▪ on ECHA list
Styrene	C_8H_8	145	▪ check standard

3.3.1   Generation of (S)VOC standards gas mixtures

For the preparation of VOC and (S)VOC gas standards two generation methods were used. However, they both needed to be modified for higher boiling compounds such as n-hexadecane, DMP and DBP, as they are less volatile and have the tendency to condense. The ultimate goal was to prepare transfer standards (i.e. sorbent tubes) containing (S)VOC amounts comparable to ambient concentrations in the range of 1-10 µg/m³. Transfer standards were produced by loading the sorbent tubes with accurately known volumes of (S)VOC standard atmospheres.

Continuous injection method

The generation method used by VSL was based on the continuous injection method according to ISO 6145-4[2]. This method allows the preparation of dynamic standard atmospheres of liquid VOCs at ppm and ppb concentration levels. The experimental set-up is showed in Figure 7. The system is based on the delivery of a constant mass flow of the liquid compound through a capillary. The liquid can be one pure compound (such as DBP) or a gravimetric mixture of different compounds (such as DBP, hexadecane and styrene). In the case of the latter all components must be soluble in each other or a suitable solvent should be used, which is not trapped by the sorbent tubes.
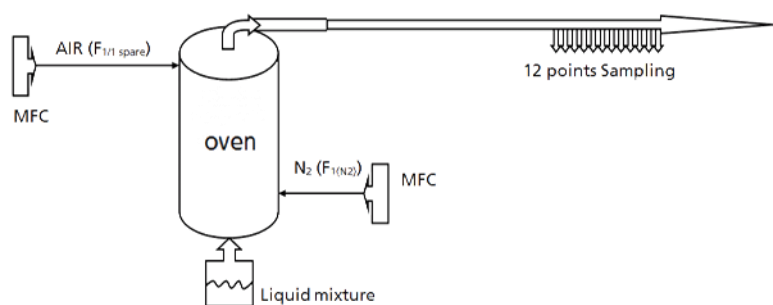

Figure 7: Set-up of the continuous injection system

The constant mass flow is obtained by applying a constant pressure to the liquid (mixture), thereby forcing it through the capillary. The mass flow was measured by weighing the loss of liquid in the reservoir. The delivered liquid flow is evaporated with a specially designed oven and the vapours are then diluted with a purified air gas stream. The gas flow stream is controlled by MFCs, each was accurately calibrated against a primary flow meter. The system included a second stage dilution system which allowed extra dilution of the generated gas mixtures down to the ppb level.

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[2] EN ISO 6145-4:2009. Gas analysis – Preparation of calibration gas mixtures using dynamic volumetric methods – Continuous syringe injection method

During preparation, styrene was used as a "reference" VOC compound to validate the preparation process. Further to this, verification of the preparation was carried out by analytical comparison using a thermal desorption gas chromatograph, equipped with a flame ionisation detector (TD/GC/FID). To do this, known amounts of the dynamically generated standard atmosphere were trapped into thermal desorption sorbent tubes and analysed against standard tubes prepared, for example, by the liquid spiking method.

Depending on the compound, the uncertainty of the VSL preparation method was estimated between 3-5 %. However, for the higher boiling compound DBP an uncertainty of 10 % was determined.

Gravimetric preparation method

NPL used the gravimetric preparation method according to ISO 6142. Due to the compounds' chemical and physical properties, this method was applicable to a selection of the targeted compounds and multi-component standards of NMP, 2-ethyl-1-ethanol and styrene in a matrix of pure nitrogen were prepared. In order to promote the use of the gas mixtures for testing, methods for the analysis of indoor air samples, such as 3-carene, o-xylene, 1,2,3-trimethyl benzene, butyl acetate, hexanal, toluene and benzene were added.

All gas mixtures were prepared in evacuated 10-litre aluminium cylinders. The cylinders were treated internally with the Air Products proprietary Experis passivation process to inhibit hydrocarbon adsorption on the walls. High concentration mixtures in the µmol/mol range (molar parts per million) were prepared using commercially sourced pure compounds. All compounds were added gravimetrically either as a gas, liquefied gas or liquid, using sequential injections from an evacuated sample loop, equipped with a valve at one end and sealed at the other. At the opening of the valve, the compound was released into the evacuated cylinder. Hence there is no compound remaining after the transfer, and therefore the mass of the transferred material can be weighed accurately. Different sized loops were used depending on the amount of material to be transferred. This procedure required the individual weighing of each compound and of the dilution nitrogen gas that filled up the gas mixture. To ensure homogeneity, the cylinder was rolled prior to analysis and further dilution to the target level. The uncertainty of the NPL's preparation method was estimated as 0.1 %.

The validation of the gas standard was performed by GC/FID and by GC/MS (mass spectrometry) equipped with thermal desorption. From the validation of the gas standard, a loss of NMP and ethyl hexanol was observed and it was concluded that adsorption or reaction of these compounds could have occurred during different stages, i.e. gas standard preparation and sampling. This effect significantly compromises both the preparation of static reference standards and their measurement. An example chromatogram is shown in Figure 8.
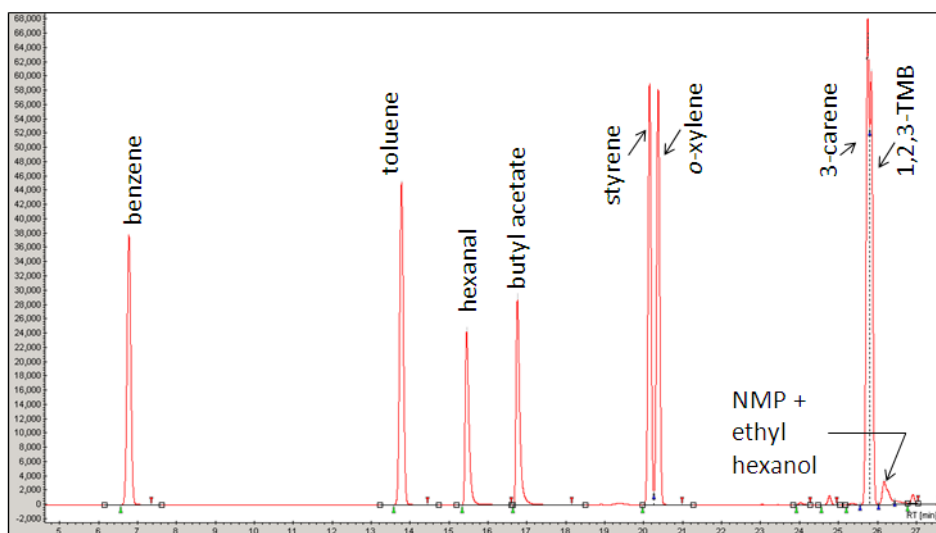
Figure 8: *Chromatogram (FID) of NPL multi-component gas mixture containing NMP and ethyl hexanol*

Further work is necessary to understand the phenomena, such as use of a different approach in the gas mixture preparation, e.g. heating of the transfer lines. In addition, adsorption and reaction effects at the surface should be thoroughly investigated to identify the most suitable materials and passivation technologies to make contact surfaces inert to these types of gases.

3.3.2 Evaluation of (S)VOC standards gas mixtures

For the evaluation of the VSL gas standards, two sets of sample tubes, filled with Tenax TA® sorbent material, were charged with a known mass of VOCs and (S)VOCs taken from a dynamically generated standard gas mixture. The two sets contained respectively 30 ng and 100 ng of each compound. The samples were analysed by BAM, NPL and VSL using their own measurement method: TD/GC/FID or TD/GC/MS. The degree of comparability between the analytical and reference values (mass loaded into the samples) was then established. *Figure 9* shows the results of each compound in the two sets of tubes.

The degree of equivalence of each laboratory was expressed quantitatively by two terms: firstly, its deviation from the reference value and secondly, the uncertainty of this deviation (at a 95 % level of confidence). The degree of equivalence between measurement standards was expressed by the difference of their deviations from the reference value and the uncertainty of this difference (at a 95 % level of confidence).

NPL did not analyse DBP, while VSL did not analyse 2-ethyl-1-hexanol. For 30 ng charged tubes NPL and BAM obtained, on average, good results with a deviation from the reference value of less than 10 % relative to the compounds analysed. With the exception of styrene, VSL's results had a large dispersion (up to 30 %), making it difficult to draw a conclusion.

For the tubes loaded with 100 ng, NPL and VSL obtained, on average good results for all components with a deviation from the reference value of less than 10 % relative for the components they analysed.

BAM underestimated the amounts of all analytes but agreed with the reference value for styrene and hexadecane. However, these results could be explained by a leak in the trap and further problems with the desorption system.

In conclusion, this comparison demonstrated that the method developed at VSL was suitable for the preparation of indoor air gas standards for the selection of VOCs and (S)VOCs. Furthermore, the measurement methods for the quantification of in indoor air were in agreement between BAM, VSL and NPL. The large majority of the results also agree within 10 % (or less) from the reference values. This comparison also highlights the challenges in standard preparation and the measurement of these compounds due to their physical and chemical properties.
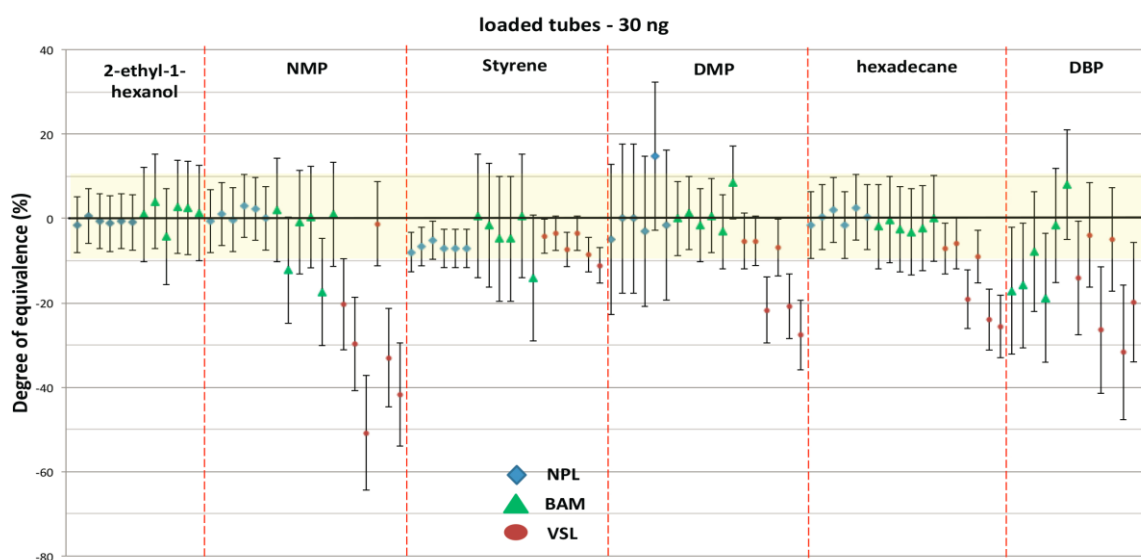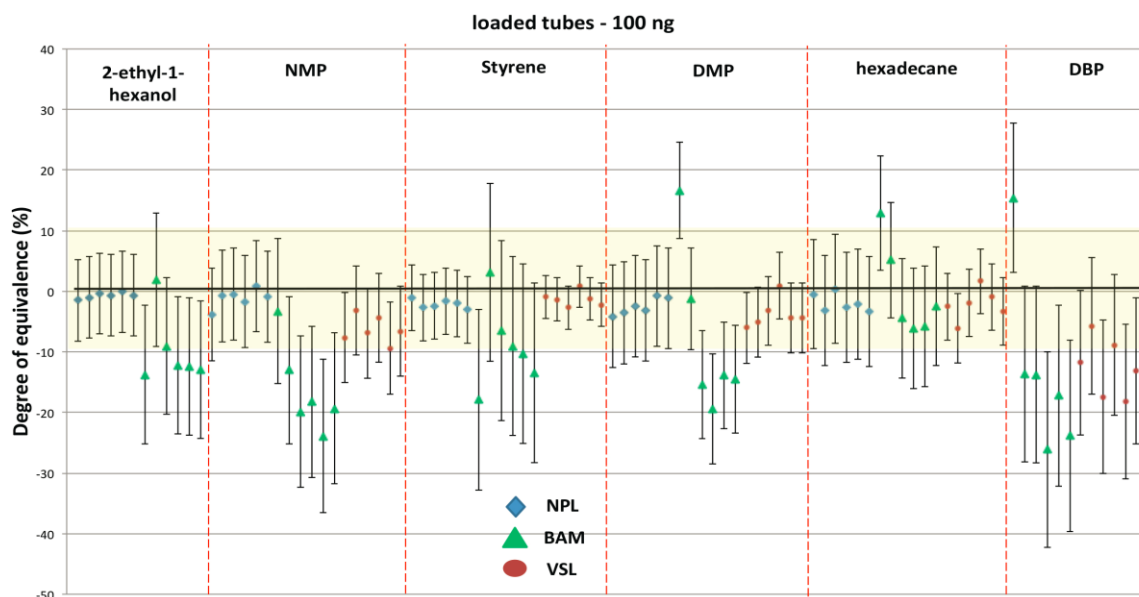
Figure 9: *Comparison of the analyses of two sets of transfer standards loaded with 30 and 100 ng of the reference gas standard prepared by VSL.*

Conclusions

This work led to the development of reference systems (gas standards and measurement methods) for a selection of VOCs and (S)VOCs, namely styrene, 2-ethyl-1-hexanol, 1-methyl-2-pyrrolidone (NMP), n-hexadecane, dimethyl phthalate (DMP) and dibutyl phthalate (DBP), measured in indoor air monitoring. The research focussed on gaining experience in preparation and analysis of SVOC, particularly relevant in emission testing and indoor air quality. The performance of the reference systems developed was confirmed by a successful comparison exercise between the project partners. The gas standards for the selected VOC and (S)VOC are now available.

3.4 Preparation of a constant emitting reference material for the quality control of emission test chamber measurements.

In order to develop a suitable reference material for reproducing the gas emission behaviour typical of a construction product, a lacquer type material was chosen as a support (carrier) for the VOCs and (S)VOCs. The advantages of this material were that it enabled high homogeneity of the VOCs mixture, relatively fast creation of a dry surface and limited emission of VOCs in gas phase from the lacquer film.

BAM purchased 12 lacquers from the same manufacturer; six were based on acryl (water as solvent) and six on alkyd (organic solvents) polymers. Additional lacquers with equal colours (clear, red, white, light-ivory) and surfaces after curing (matt, glossy) were also selected. The first step consisted of testing the lacquers' self-emissions. However, analysis with gas chromatography (GC) for the alkyd lacquers showed large amounts of emissions in the range of the chromatogram where VOCs would elute, and for this reason the alkyd lacquers were discarded and the study concentrated on the acrylic based lacquers.

Samples were prepared by weighing portions of lacquer and decanting them into 100 mL screw cap bottles. Defined amounts of the pure analytes were then added using gas-tight syringes under simultaneous magnetic stirring. The mixture was then agitated for 1 h in the closed bottle, and defined amounts of the lacquer mixture were filled into Petri dishes (Ø 33 mm). After preparation, aliquots of each batch were immediately loaded into the six chambers of a micro-chamber and thermal extractor device (µ-CTE®, Markes) and left to cure for one hour. Each µ-chamber was purged with the same constant flow of pure air passing over the samples and sweeping emitted VOCs onto thermal desorption tubes connected to the outlets. The µ-CTE temperature was set to 25 °C and a flow of approx. 30 mL/min was applied.

The criteria for the selection of the "most" suitable lacquer were the surface conditions and the emission rate, which ought to be as high as possible. When comparing the water-based lacquers, it results showed that the clear and glossy one (WGC) fulfilled the criteria. The remaining lacquers had lower compound release rates or created fissures at the surface which seriously affected the emission behaviour (See Figure 10).

Figure 10: Comparison of the dry surfaces of a red matt, white matt and clear glossy lacquer

Further and important requirements for the production of the reference material were repeatability (homogeneity), reproducibility and the influence of test chamber parameters, such as air flow velocity and relative humidity (RH), on emission rates.

To determine the reproducibility (relative standard deviation (RSD repro)) of compound emissions from spiked lacquers, three 50 g samples of WGC were spiked with all six selected VOCs (see Table 1). Six 2 g aliquots of each of these three spiked lacquer samples were then transferred to Petri dishes and loaded subsequently into the µ-CTE such that all six chambers contained a sample, and any deviation in emissions between each of the six chambers could be determined. This deviation, averaged over three batches, indicated the relative standard deviation of repeatability (RSD repeat). Samples were collected on days 2, 4, 7, 9 and 11 after loading (See Table 2).

Table 2: Average (AV) and relative standard deviation (RSD(repro)) of three identically prepared spiked lacquer samples over different sampling days; RSD(repeat) stands for the mean RSDs measured in one µ-CTE over different sampling days

n=3 lacquer-batches		styrene	E.H.	NMP	DMP	C16	DBP
2 d	Mean [µg/(m²h)]	1500	1000	4800	850	980	20
	RSD(repro) [%]	5	26	15	4	7	27
	RSD(repeat) [%]	1	32	4	8	7	21
4 d	Mean [µg/(m²h)]	410	160	1900	720	740	21
	RSD(repro) [%]	3	35	16	5	7	39
	RSD(repeat) [%]	3	15	3	8	6	23
7 d	Mean [µg/(m²h)]	100	77	1000	760	710	35
	RSD(repro) [%]	1	34	17	5	9	13
	RSD(repeat) [%]	4	6	7	8	7	13
9 d	Mean [µg/(m²h)]	32	75	670	700	630	27
	RSD(repro) [%]	2	20	18	3	9	18
	RSD(repeat) [%]	10	8	10	7	5	13
11 d	Mean [µg/(m²h)]	< LoQ	44	460	670	560	25
	RSD(repro) [%]	< LoQ	9	18	7	12	14
	RSD(repeat) [%]	< LoQ	10	15	7	6	13

The results of the repeatability and reproducibility were indicative of the homogeneity of the lacquer with respect to emissions which was a fundamental requirement for the reference material. Between the three batches of lacquer, emissions of styrene, DMP and C16 were reproducible with RSDs below 10 %. For NMP the uncertainty was slightly higher at just below 20 %. After a delay time of approx. seven days the RSD of DBP emissions stabilise below 20 %.

Relative humidity and air flow in a chamber can affect the emission rate and this was observed for hexadecane and NMP and may be explained by their polarity. At dry chamber air (0 % RH) NMP as the most polar compound showed high emission at an earlier stage compared to when the flow was humidified (55 % RH). This was because the evaporation of the solvent water is supported by dry air. The same applies for higher air flows through the chamber, as the higher it is, the faster is the curing of the lacquer surface. The opposite was observed for hexadecane as the most non-polar compound and the emissions of the other compounds (styrene, 2-ethyl-1-hexanol, DMP, DBP) showed almost no affect.

Conclusions

The aim of this work was to prepare a constant emitting reference material for the quality control of emission test chamber measurements. The results were the first study on the production of a reference material for the quality control of emission testing of VOCs less volatile than toluene[3]. A water-based clear lacquer that created a glossy surface (WGC) was found to be provide the most suitable support (carrier) for reference materials. It combined both a homogeneous surface after curing and high analyte release with low self-emission. All VOCs had a wide range of polarity and volatility emitted from the lacquer system in easily detectable amounts/rates. After 7 days, emission rates were reproducible with variations of less than 20 %. So far the reference material has been successfully used as sample for an interlaboratory comparison between emission testing laboratories. A new EMRP project, ENV56 KEY-VOCs, will continue this work experimenting with other types of support to improve the reproducibility of the VOCs emission.

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[3] M. Nohr, W. Horn, K. Wiegner, M. Richter, W. Lorenz. Development of a material with reproducible emission of selected volatile organic compounds - µ-chamber study. Chemosphere, 107 (2014), 224-229.

3.5   Development of an evaluation protocol to verify the performance of micro-sensors as an "indicative method" according to the Air Quality Directive and of QA/QC procedures for the calibration of sensors. The project also focussed on the assessment of the performance of a selection of micro-sensors for the measurement of specific air pollutants.

3.5.1   Testing protocol and testing of the performance of ozone and nitrogen dioxide micro-sensors

Testing protocol

Gas micro-sensors have been identified as emerging measuring devices for "indicative measurements" regulated in the Air Quality Directive (2008/50/EC) and compared to reference measurements they could provide lower cost air pollution monitoring. The Air Quality Directive requires demonstration that indicative methods can meet a data quality objective (DQO) that is approximately twofold less stringent than the one for reference methods. However, as the Directive does not give any guidance for this demonstration, the MACPoll project developed a protocol for the evaluation of micro-sensors (developed by the JRC and REG(CSIC)) (See Figure 11).

The micro-sensor evaluation was carried out against a limit value (LV) defined in the Air Quality Directive with a corresponding averaging time for each air pollutant. The selection of the micro-environment (urban, rural or suburban areas for background, traffic or industrial monitoring sites) in which the micro-sensor will be used then allows the estimation of the operating range of the micro-sensor, the abundance of possible gaseous interferences, the temperature and relative humidity of exposure. An exposure chamber, built at JRC, was used for testing the micro-sensors (See Figure 12). This system allowed the measurement, control and change of the concentration of the test gas, temperature, relative humidity, wind velocity and added gaseous interferences. The evaluation of micro-sensors used the comparison between micro-sensor responses and reference measurements.
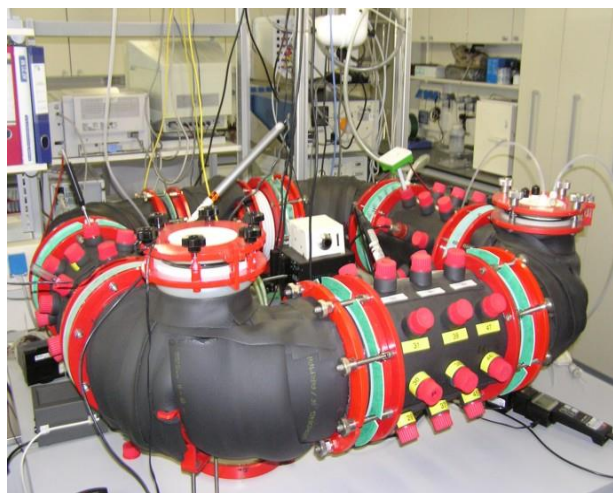

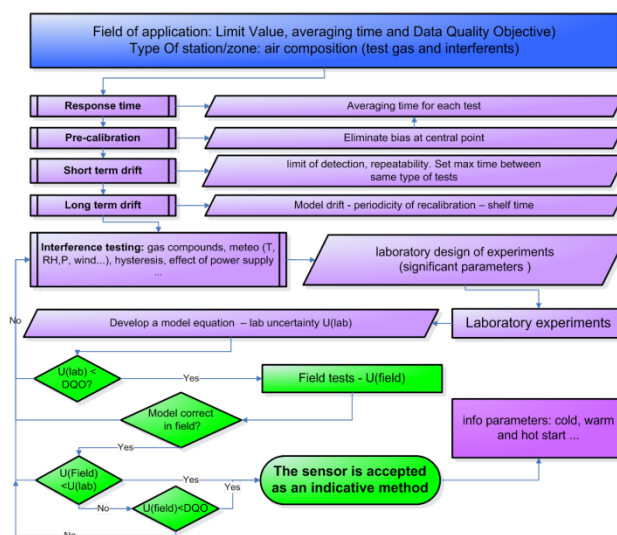*Figure 11: Protocol for evaluation of micro-sensors*   *Figure 12: Exposure chamber for micro-sensor tests*

The protocol uses as a first step the measurement of the response time of the micro-sensor to a specific air pollutant and therefore the evaluation of the averaging response time to reach stability. Following this, a pre-calibration of the micro-sensor is performed at several concentration levels over the full scale in order to eliminate any bias at the mean exposure conditions. Hysteresis is then evaluated by consecutively repeating the pre-calibration in an increasing ramp, a decreasing ramp and an increasing ramp of test gas. Subsequently, repeatability and the short and long term drifts of the micro-sensor are determined. Repeatability imposes limits on the accuracy of the calibration and the short term stability is used to set the maximum time between similar tests. According to the testing protocol, the next step is the identification of significant gaseous interfering compounds including the matrix effect (filtered air, laboratory air and ambient air) as well as the effect of temperature and humidity and physical parameters e.g. ambient pressure, power

supply and wind velocity. Finally a full factorial experiment is set up using the test levels used for pre-calibration. The factorial experiments include testing at three different temperatures, under three levels of relative humidity and at two levels of any parameter found to be significant in the previous experiments. Any significant effect found can be corrected in the model equation or treated as an uncertainty contribution. The measurement uncertainty of the micro-sensors studied in "laboratory conditions" is then estimated with the results. A gas micro-sensor was deemed not suitable as an "indicative method" of the Air Quality Directive when the measurement uncertainty in "laboratory conditions" exceeded that given in the DQOs.

The developed testing protocol included measurements in "field conditions". An appropriate test site, a typical location where micro-sensors could be located, was selected. A test of at least three months should be carried out which included periods representative of the extremes conditions likely to be encountered in the selected micro-environment of the micro-sensor. The monitoring site should also be equipped with a gas analyser, accepted as a reference method, in order to simultaneously measure the air pollutant concentrations under investigation. The measurement uncertainty of the micro-sensor under field conditions was calculated by comparing the micro-sensor results with the reference measurements. A gas micro-sensor was deemed acceptable as an "indicative method" of the Air Quality Directive if measurement uncertainty in "field conditions" did not exceed that given in the DQOs.

Testing of ozone and nitrogen dioxide micro-sensors

Based on the testing protocol, the performance of a selection of micro-sensors for the measurement of ozone and nitrogen dioxide was assessed. The list of tested micro-sensors is given in Table 3. They were classified in two families:

1   the chemical sensors (Chem.), a miniaturised electrochemical cell able to deliver a current varying with the level of the pollutant of interest and

2   the metal oxides sensors (Resistive or MOx) based on the variation of the resistance of a semi-conductor that changes with the concentration of the pollutant being monitored.

In addition, the micro-sensor based on graphene and developed in this project was tested for NO_2.

Table 3: The tested ozone (O_3) and nitrogen dioxide (NO_2) micro-sensors

	Manufacturer	Model	Type
O_3	Citytech – DE	Sensoric O3E1 and O3E1F sensors	Chem. 3 electrodes
	CairPol – FR	CairClip O_3/NO_2	Chem. 3 electrodes
	αSense - UK	O_3 sensors (O3B4)	Chem. 4 electrodes
	SGX Sensortech – CH	MiCS-2610 and Oz-47 sensors, OMC2 and OMC3 sensors	Resistive
	IMN2P – FR	Prototype WO3 sensor	Resistive
	FIS - JP	SP-61 sensor	Resistive
	Unitec s.r.l – IT	O_3 Sens 3000	Resistive
	Ingenieros Asesores – SP	NanoENvi mote	Resistive
NO_2	Citytech – DE	Sensoric 3E50 and 3E100 sensors	Chem. 3 electrodes
	CairPol – FR	CairClip NO_2	Chem. 3 electrodes
	αSense - UK	NO_2 sensors (B4)	Chem. 4 electrodes
	SGX Sensortech – CH	MiCS-2710 and 4514 sensors	Resistive
	MIKES – FI	Prototype graphene sensor	Graphene

For O_3, the response time showed that on average the chemical sensors (1.3 min) were faster than the resistive ones (40 min). For NO_2, the chemical sensors gave on average a response time of 6.5 min and a response time of over 60 min for the resistive sensors. On average, both types of sensors were slower in response time when decreasing of the pollutant level.

While chemical sensors generally showed linear calibration lines (raw sensor responses versus pollutant levels), the metal oxides gave resistances varying with parabolic/cubic, exponential or logarithmic patterns.

In general the repeatability of sensors was good, in the range of 1 to 2 ppb for the best sensors and up to 4-5 ppb for the worst ones. However, for a few chemical sensors, the scattering of their responses increased

towards zero thus increasing the limit of their detection. Good short term stability was generally observed demonstrating that within 48 hours the response of the sensors can be expected to be constant. The long term trend of sensors (between 60 to 200 days) was rather flat for O_3 chemical sensors while strong random drift was observed for resistive sensors. For NO_2, linear drift was observed for chemical sensors both depending on time and the NO_2 level, whilst again random drift was observed for metal oxide sensors.

Among O_3, NO_2, NO, CO, CO_2, NH_3 and SO_2, the most significant gaseous interference occurred in the lack of selectivity between O_3 and NO_2 for the chemical sensors with a sensitivity coefficient close to 1. Without correction this interference may prevent correct estimation of O_3 or NO_2. However, it should be noted that one manufacturer of chemical sensor succeeded in solving this problem by filtering one of the compounds. For the O_3 MOx sensors, nearly no gaseous interfering compound was found, but NO_2 MOx sensors where highly affected by O_3 and slightly by CO.

Generally temperature and humidity affected all sensors to different extents, the effect being generally linear for resistive sensors and a hysteresis loop for the chemical sensors (that was difficult to correct). Again some manufacturers solved problem by data treatment or by filtering the humidity effect. However, the sensors also appeared to be slightly influenced by wind velocity, hysteresis and matrix effect. Conversely, a change in pressure or power supply had no effect on the sensor response and it is likely that the non-sensitivity towards power supply is due to the quality of the DC transformer used in laboratory tests.

In "laboratory conditions" simple models were established to compute O_3 and NO_2. In general, the measurement uncertainty in "laboratory conditions" easily met the DQO for chemical sensors, but not always for resistive sensors. Unfortunately, the laboratory models were not found to be effective during "field measurements/conditions". Only one O_3 chemical sensor, the one where the manufacturer solved the problem of NO_2 interference and humidity hysteresis was able to reach the DQO of indicative methods using field calibration. The NO_2 sensors were found to be too sensitive to O_3 during "field measurements/conditions" to reach the DQO for NO_2. This maybe because the "field measurements" took place in spring/summer season and winter may have been more suitable.

3.5.2   Cluster of sensors

Based on the results of the evaluation and validation of O_3 and NO_2 micro-sensors, several sensors were grouped in a clustered system able to measure NO/NO_2/NOx, CO, SO_2 and O_3 (air pollutants regulated in 2008/50/EC). To extend the range of species, CO_2 sensors and PM2.5 and PM10 personal aerosol monitors were added. The developed cluster of sensors consisted of different types of sensors: 4 NO_2 sensors and 2 CO sensors, both electrochemical and metal oxide type, 1 NO and 3 O_3 electrochemical sensors, 2 infrared CO_2 sensors and 1 PM2.5 and 1 PM10 nephelometers. The performance of the clustered sensor system was evaluated, as well as different calibration methods.

Several calibration methods for micro- sensors were compared using data from a measuring campaign. During this campaign, NOx, O_3, CO, CO_2 and SO_2 concentrations data were collected from the clustered senor system and from reference gas analysers. At the same time meteo data (temperature, relative and absolute humidity, wind and pressure) was recorded.

Single calibration methods included: simple linear models (LR), multi linear regression models (MLR) established in previous laboratory studies and Artificial Neural Network (ANN) with raw, standardised and calibrated (MLR) sensor responses. The performance of each calibration method was compared taking the measurement uncertainty as an indicator of the calibration efficiency. Based on the measurement uncertainty estimated with orthogonal regressions of the estimated outputs versus reference data, the best calibration method appeared to be ANN using calibrated sensors. ANN using a cluster of only 3 sensors of different types (1 O_3 chemical and 2 NO_2 resistive sensors) was able to solve the NO_2 interference on the O_3 sensor and to assure independence to the meteo parameters. In contrast simple LR was shown to produce high measurement uncertainty and MLR needed meteo data for calibration of most sensors.

Regarding the calibration methods, it was observed that the Partial Least Square (PLS) methods with and without meteo data resulted in a larger measurement uncertainty than for ANN methods. The use of meteo data resulted in an overall reduction of the measurement uncertainties, but was more pronounced for ANN than for the linear PLS. This was probably due to the fact that the influence of the parameters is complex and nonlinear, as the ANN method increased the strength of association between estimates and reference data (higher R^2 and lower Residual Standard deviation RSS and hence lower uncertainty). Within the ANN methods, the method using input from a physical model was better than ones using only meteo data, only PLS or meteo data plus PLS regressions. In conclusion, the ANN calibration method combined with meteo

data and the physical model (whose parameters were determined by multivariate regression PLS) was the most suitable calibration method.

The data quality objectives of the European Air Quality Directive for indicative methods could be met for O_3 (uncertainty, Ur, of 30 %) and likely for CO (Ur of 25 %). However, the DQO for SO_2 could not be evaluated as the registered levels were too low. For NO_2, it is unlikely that the DQO (Ur = 25 %) could be met and we expect an uncertainty of approx. 35 % at the limit value of 100 nmol/mol. In addition to this, the NO measurements with cluster of sensors were rather poor, the best result being an uncertainty of approx. 75 %. In contrast for CO_2, a very low uncertainty, down to approx. 3% was reached.

Conclusions

This work led to the development of an evaluation protocol to verify the performance of micro-sensors as an "indicative method" according to the Air Quality Directive and of QA/QC procedures for the calibration of sensors. The project also focussed on the assessment of the performance of a selection of micro-sensors for the measurement of specific air pollutants. The objectives of this part of the research have been met; an optimised an evaluation protocol was developed for the assessment of gas sensing devices for air monitoring in laboratory and in field conditions. The protocol was then used for the evaluation of ozone and nitrogen dioxide gas sensors and for the evaluation of a cluster of sensors measuring several air pollutants. The results indicated that sensors tested in laboratory and field conditions behave differently, therefore gas sensors need to be accurately validated before entering the market. In addition, further research in gas sensing technology is needed to be able to measure simultaneously the air pollutants according to data quality objectives of the European Air Quality Directive.

3.6   Development of a new highly sensitive and selective NO_2 sensor using the 2-D material graphene

Graphene is a promising material that has unique properties like high surface-to-volume ratio, low electrical noise, and exceptional transport properties associated with its unique two-dimensional structure. The adsorption ability and wide surface area of graphene also make it attractive as a gas sensing material.

Within the MACPoll project, MIKES, INRIM and REG(Aalto) chose to exploit graphene technology in order to develop small scale NO_2 gas sensors with very high sensitivity. To begin with the effect of NO_2 adsorption was investigated by studying the evolution of the fabrication technology and the post-fabrication procedures. Then they improved the sensing abilities to NO_2 gas traces and electrical characteristics of the fabricated graphene based gas sensors. During development the graphene sensor design was modified according to the results of preliminary gas sensing measurements.

3.5.3   Epitaxial graphene

Current gas sensing experiments have demonstrated that epitaxial graphene films are an excellent material for developing NO_2 sensors. Graphene layers grown on SiC substrate have demonstrated sensitivities down to parts per billion (ppb) levels, and shown stability for NO_2 detection with respect to typical interfering gases.

The project found that optimisation of the structure of design of the sensor, of the used materials, and electronics, together with improvement of the contact metal/graphene significantly improved the stability of the sensors and increased the sensitivity of the developed sensors.

The graphene sensor construction consisted of a chip with graphene films which was assembled on a TO-8 holder together with a heater and Pt100 temperature sensor. The current channels of the sensor devices were oriented along the atomic terraces on the graphene surface according to AFM imaging, as terrace-oriented devices demonstrated superior performance compared to randomly oriented devices. The contacting area graphene/metal was modified so that the double layer metal-graphene contacts were implemented in the device.

For testing the sensor's sensing ability, Teflon based enclosures were fabricated and used. For measurements of a sensor response to NO_2, a custom made gas system was used. NO_2 gas (originally diluted to 10 parts per million (ppm) with air) was mixed with dry (relative humidity 0,02%) air by using a two stage dilution system based on mass flow controllers (Aera FC-D980). The dilution ratio was varied in the range 1:1–1:106, providing an output concentration in the range of 0.01 ppb to 10 ppm. Configuration of the sensing elements was done so that the used sensor (placed on one sensor chip, of 5x5 mm) had six sensing devices, which were connected in series, and the response from each of the sensors was acquired simultaneously, providing more reliability of the measured signal.

In *Figure 13* is shown the response of an as-prepared graphene sensor to exposure of NO_2 gas at room temperature (exposure periods are marked as grey bands, in the 0.2 ppb – 2 ppb concentration range). It is known that epitaxial monolayer graphene is originally n-doped and NO_2 is known as a strong oxidiser, withdrawing electrons from the surface on which it adsorbs. Therefore, the adsorption of NO_2 on a graphene surface is expected to reduce the density of electrons in the case of n-type material, thus leading to an increase in resistivity and a response that has an integrator-like behaviour. Under NO_2, exposure resistivity linearly increases with time, with the slope of the curve being proportional to the NO_2 concentration. However, when gas exposure is interrupted the resistivity remains practically constant without significant recovery. Such behaviour indicates a relatively strong bonding of NO_2 molecules to the graphene surface.

The resistivity of the graphene devices strongly decreased from approx. 30 kΩ to 15 kΩ after annealing at 120 °C in the carrier gas flow. A possible reason for this, could be thermal desorption of the contaminations remaining on the sensor surface after the fabrication process. In Figure 14 and *Figure 15* is shown the response of the annealed graphene sensor to the exposure to NO_2 at room temperature for low and high concentrations, respectively. The response of the annealed sample becomes approximately tenfold stronger compared to that of an as-prepared sensor.

In Figure 14 and *Figure 15*, at the ppb concentration range, due to short exposure time and relatively low NO_2 concentration, there are no visible signs of saturation on the response curve. Similarly for the as-prepared sensor a linear increase in resistivity was observed during exposure, the slope of the response
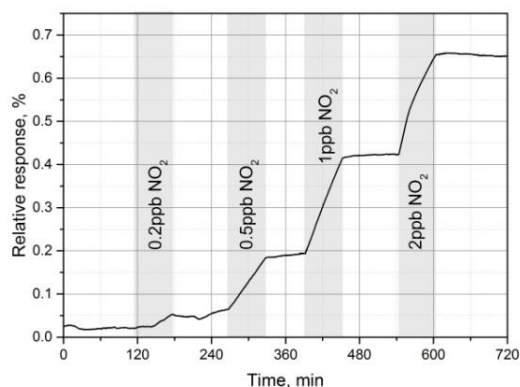
Figure 13: *Response to exposure of gas mixture containing NO$_2$ at room temperature for as-fabricated graphene based sensor*
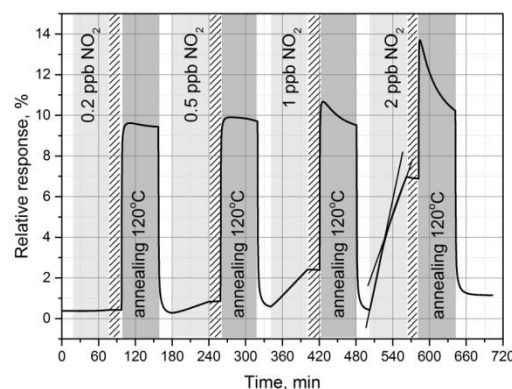

Figure 14: *Response to exposure of gas mixture containing NO$_2$ in the low concentration range at room temperature for the annealed graphene based sensor. Knee on response curve is highlighted by two additional lines*
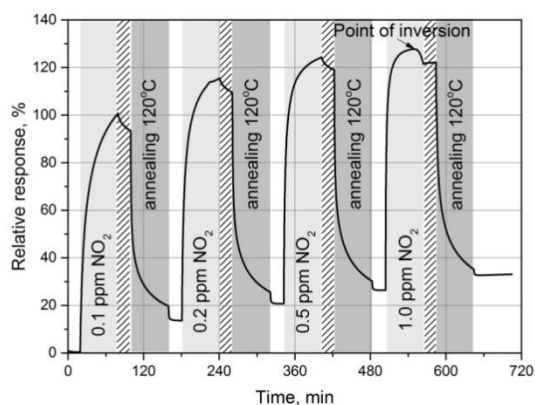

Figure 15: *Response on exposure to the gas mixture containing NO$_2$ in the high concentration range at room temperature*

Starting from 2 ppb of NO$_2$ concentration a small knee appears on the response curve, (see Figure 14) which may indicate the existence of two different types of adsorption centres: low-energy adsorption centres of graphene (sp2 -bonded carbon) and high-energy adsorption centres like oxygen groups and defects. The concentration of the different types of defects and therefore the high-energy centres can be relatively high according to Raman spectroscopy.

When the graphene sensor was exposed to lower concentrations of NO$_2$, the adsorption centres with a high binding energy are occupied first. However, as soon as they are filled, the centres of adsorption with low binding energy begin to dominate the gas response. This hypothesis is supported by the recovery behaviour of the graphene sensor following exposure to different gas concentrations. After low concentrations the response curve is nearly horizontal (See Figure 14, hatching bands after exposure periods with 0.2, 0.5 and 1ppb concentrations), which indicates no desorption due to the strong binding of NO$_2$ molecules. Whilst at higher gas concentration the desorption becomes significant, which indicates weaker binding energy (See Figure 14, 3 hatched bands after exposure periods with 2 ppb, 0.1, 0.2 and 0.5 ppm).

The value of the response is proportional to the gas concentration in the wide (50 ppb-1 ppm) range. The response of CVD based devices on NO_2 exposure is significantly less, compared to the response with SiC and is typically is a few percent for NO_2 concentrations in ppm range. The detection limit of the graphene sensor was estimated to be 0.6 ppt (part-per-trillion). In conclusion, the fabrication of graphene sensors based on epitaxial graphene with additional annealing improves the performance of graphene based sensors and make them suitable for environmental nitrogen dioxide gas monitoring.

3.5.4   Exfoliated graphene

This fabrication method exploited the most common techniques used in the semiconductor industry: photolithography and electron beam lithography (EBL), which allowed the development of structures with a size down to few tens nanometers. Both photolithography and EBL are based on the same principle: the interaction between a polymer and UV-light or e-beam which makes the exposed portions of the polymer soluble in particular solvents and leaves behind the unexposed parts. The techniques allow the carving of structures that are the starting base for the subsequent realisation of microscopic structures. However, these processes need to be performed with care over the control of the substrate surface quality in order to minimise the lithographic process steps and avoid contamination, as this controls the native doping level of the deposited graphene and achieves higher electron mobility.

An annealing process was optimised in order to recover the sensor performance. Further experiments were carried out on the sensor in order to investigate its behaviour in the presence of NO_2 at various concentrations ranging from 100 nmol/mol to 10 µmol/mol. Sets of measurements to evaluate the interference of gaseous species as H_2O (200 ppm), CO_2 (400 ppm) and NH_3 (10 ppm) showed that they all affected the graphene sensors.

The optimisation of a plasma process for functionalising the graphene-based sensors with polyethylenediamine was also performed. The aim of the functionalisation was the enhancement of the sensor selectivity toward NO_2. The first results showed that even if an enhancement of an order of magnitude in the sensor response to NO_2 at a concentration of 100 nmol/mol was recorded, it did not demonstrate clear effectiveness of the functionalisation process. A second functionalisation process was therefore carried out and showed satisfactory results in terms of response enhancement. However, significant noise was detected, probably due to damaging of the electrical contacts of the sensor due to extensive use.

Conclusions

The aim of this work was the development of a new highly sensitive and selective NO_2 sensor using the 2-D material graphene. The potential graphene technology was explored by two groups (MIKES/Aalto University and INRIM) independently. The objectives of this part of the research were met. Graphene sensors prototypes for the measurement of nitrogen dioxides were constructed. Although these sensors were very sensitive to low NO_2 levels, they were affected by interferents as well as by difficulties in resetting their response after exposure. Therefore these sensors were optimised after testing and the latest versions of the prototypes now show good sensitivity and improved gas selectivity.

4   Actual and potential impact

4.1   Dissemination activities

4.1.1   Scientific publications

This project has generated eleven peer reviewed publications and the list is available in section 6.

4.1.2   Presentations

The project's activities and results have been widely disseminated in targeted scientific events such as *NOSE*, *GAS* and *CPEM* and in events for a broader audience such as the *Int. Congress of Metrology* and *Pittcon*. In total 54 oral presentations and 21 posters presentations were given by the project partners and grant researchers at conferences, workshops, seminars and self-organised events. MACPoll project results are still being presented after the end of the project and at, at least eight other international conferences. It should be noted that the project coordinator gave a key-note lecture at the 7th Gas Analysis Symposium (Rotterdam, NL, 2013) and a number of project partners were invited speakers at meetings and workshops such as the *EPA's Next Generation Monitoring Workshop series* and the *EuNetAir meetings*.

4.1.3   Organisation of dedicated scientific events

During the project, a stakeholders' 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. In total, 24 lectures and 11 posters presentations related to the project activities and results have been given. All these events were well received and provided excellent interaction opportunities with stakeholders and end-users.

Experts from specific fields related to the project were invited to give lectures at these events. For example the following experts represent a selection of the invited speakers:

- for the workshop on zero air the chairs of ISO/TC 158 "Gas analysis" and of AQUILA (European Air Quality Reference Laboratories) network,

- for the workshop on ambient air the chair of EuNetAir network (European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability - COST Action TD1105) and

- for the workshop on indoor air an expert from Cranfield University, UK.

The final, very successful event was the MACPoll final conference, held at VSL's premises in May 2014. This conference disseminated the project's technical outputs through the combination of oral and poster presentations and laboratory demonstrations. Stakeholders and end-users from air quality laboratories, monitoring networks, standardisation bodies and manufacturers of gases, sensors and equipment attended the event. Some participants presented posters, such as the University of Nijmegen and the Japanese gas manufacturer Takachiho, and some gave a laboratory demonstration, such as the equipment manufacturer LNI Schmidlin and the gas sensors manufacturer CAIRPOL (*Figure 16* a,b).
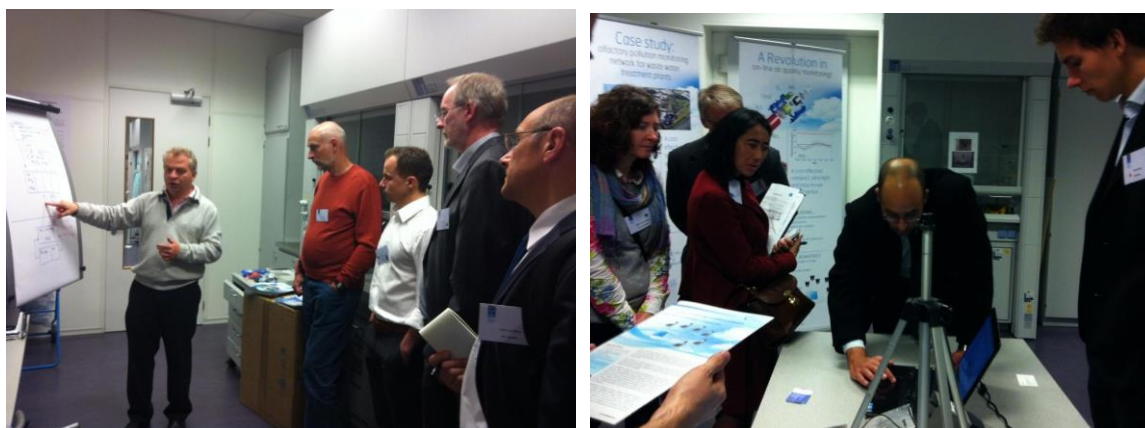

Figure 16 a,b: *Stakeholders demonstrations at the MACPoll Final Conference: LNI-Schmidlin (11a) and CAIRPOL (11b)*

4.1.4   Engagement with standardisation and metrological committees

The project's successful engagement with standardisation and metrological working groups (WGs) benefitted from the active participation of the project partners in these committees. Due to this, the project outputs have been regularly presented at the following European and international committees:

- ISO/TC158/WG5 "Gas analysis- dynamic methods",
- CEN/TC264/WG12 "Air Quality-Reference Methods",
- CEN/TC351/WG2 "Emission from construction products into indoor",
- EURAMET-METCHEM Gas subcommittee (MC/GASC)

In addition, the project activities have also been discussed at a national level, in the air quality and gas analysis standardisation working groups.

During the project, a number of deliverables were prepared in the form of "Guides" and "Protocols" to be submitted to the relevant technical WGs. Three guides on dilution methods for the preparation of calibration gas mixtures of reactive pollutants at EU limit values have been distributed within ISO/TC158/WG5. These guides will be very useful for the revision of documentary standards prepared by the WG, such as ISO 6145 series and ISO 6144. The outcome of the research on zero gas "Certification protocol for zero gases" will provide input for a new working item within the same ISO/TC158 committee. However, because of time constraints, it was agreed to wait for the revision of the standard before including the project's input.

Of special interest is the work carried out on the evaluation of gas sensors. This project output has initiated a discussion amongst CEN/TC264 on the need to initiate standardisation activities for the use of gas sensors in air monitoring.

In addition to this, the results of the comparison organised to demonstrate the comparability of calibration gases for reactive pollutants (see section 3.1.2) was presented at the EURAMET MC/GASC (Teddington, February 2014). Based on these results and during the meeting, it was decided that a new comparison for SO_2 with concentrations targeted at EU limit values, was necessary. This comparison, EURAMET 1329, will be coordinated by LNE and it is open for participation to all GASC members.

Finally, the interest of the standardisation and metrological experts in the project, was clearly demonstrated at the MACPoll final conference, which was attended by representatives of ISO/TC158, by the members of CEN/TC264/WG12 and of EURAMET- METCHEM.

4.1.5   Engagement with stakeholders

All project partners have actively engaged with project stakeholders and end-users thanks to their membership of key environmental networks (e.g. the *AQUILA* European network), their participation with standardisation activities, their collaboration with National Environmental Institutes and their provision of traceable calibrations standards to air quality monitoring networks. During the project, partners and stakeholders have exchanged information on a regular basis at events (workshops, meetings) organised by both parties.

At the core of the project's engagement with stakeholders, was the opportunity for them to become advisors or project collaborators. This provided discussions on the progress of the project activities and exchange of scientific information. The AQUILA network also helped the project partners to better understand the issues of measuring in the field. In return, this network is benefiting of the project results as they help improve the measurement of chemical air pollutants in Europe and therefore the enforcement of the Air Quality Directive.

For other 'newer' stakeholders, such as the *EuNetAir* network, this engagement has turned into a productive collaboration which will continue beyond the project's life time. In particular, the collaboration between the project partner JRC (EC, Joint Research Centre located in Ispra - Italy) and ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development) the institute chairing the EuNetAir network, has led to the preparation of a poster "*Calibration of a cluster of low-cost sensors for the measurement of air pollution in ambient air*" which was been judged as the best poster at the MACPoll Final Conference (*Figure 17*). This collaboration was also advertised in a videoclip of the Geo&Geo TV program broadcasted by the Italian channel (RAI) on 25 February 2014.

Figure 17: *Prize giving at the MACPoll Final Conference. From right to left: winners (JRC and ENEA) at the poster award and the MACPoll coordinator*

Sixteen out of thirty of the project's stakeholders were international gas producers companies, purification systems and gas sensors manufacturers. They officially become project collaborators and have been following closely the progress of MACPoll. Their interest and active engagement to the project is demonstrated by their participation at MACPoll events and in particular the final conference. Most groups of these manufacturers provided not only their scientific expertise but also offered their equipment for testing. Manufacturers of zero gas generation systems (LNI Schmidlin and Environics) and purification system producers (SAES and NuPure) provided their products as well as different gas sensors manufacturers sent their prototypes for testing. The results of such testing provided important feed-back for the manufacturers, so that they could gain confidence in their products' reliability and use the information as a basis for further improvement.

The project's dedicated scientific events, attracted between 30 and 50 European and international stakeholders and end-users per event, which gives a good overview of their external participation/involvement in the project outputs.

4.1.6   Other activities

The MACPoll project has attracted interest from the academic community and during the project two master students produced their final thesis and one had a six months internship under the supervision of the project partners (MIKES, BAM and VSL).

At the begin of April 2014, JRC also provided external training on "gas mixing system and sensor validation tests" at the 2nd training school held at Saarland University, Saarbrucken (D). This event was organised by EuNetAir.

4.2   Cooperation between the project partners and researchers

All technical activities have been successfully completed thanks to the commitment and contributions of all project partners and researchers. Several presentations and publications prepared by the project are the result of such cooperation. However, the organisation of the MACPoll final conference is the best example of this collaboration, where everyone contributed with ideas and inputs to the preparation of joint lectures, posters and demonstrations.

The organisation, participation and subsequent discussions of the project's two comparison exercises (for reactive gases and for (S)VOCs) also clearly demonstrated the sharing of experience and knowledge between project partners; as did the secondment of Olavi Vaittinen, the researcher from the University of Helsinki (FI), at VSL for the work on the measurement of NH_3 by CRDS. The secondment helped both parties in improving their measurement systems.

Other important examples are the collaborations of partners and researchers from different fields of expertise that led to the development of project outputs that were not realisable by one single NMI. Such as the development of the "Certification protocol for zero gas standards" which brought together experts in laser spectroscopic techniques (VSL, PTB, MIKES, LNE) and conventional analytical techniques (NPL, IL, SMU).

This project also created new, unplanned collaborations, such as three project participants from Finland (MIKES, IL and Aalto University) who collaborated on the testing of a graphene-based sensor for NO_2 and ozone monitoring. Further examples were part of EMRP researcher mobility grants; where researchers from the Turkish Metrology Institute (TUBITAK) and from the Serbian Directorate of Measures and Precious Metals (DMDM) spent respectively six and three months at VSL on the development of ultra-low standards gas mixtures of NO_2 and NO for the MACPoll activities on zero gas standards.

4.3   Intermediate impact

4.3.1   Standards and regulation

The outcome of the research on zero gas "Certification protocol for zero gases" will provide input for a new working item within the same ISO/TC158 committee. However, because of time constraints, it was agreed to wait for the revision of the standard before including the project input.

Due to its affinity with research in the field of ambient air pollution linked to the European Air Quality Directive, this project was invited by the DG RTD to provide input for a report on research findings relevant to a revision of the European Air Policy.

4.3.2   User uptake

The MACPoll project has had a direct impact on NMIs and Designated Institutes dealing with the measurement of trace level gases. The project has helped to improve the measurement capabilities of these organisations in terms of better standards and lower uncertainties. A number of project partners are designated Air Quality National Reference Laboratories (NRLs) and the project results have been beneficial for their task of ensuring traceability and comparability to the air monitoring networks as required by the EU Air Quality Directive.

The new reference materials and methods for indoor air, developed by the project, have been implemented by the emission testing laboratories dealing with the emission of hazardous components from building materials. The results have also been used in two interlaboratory comparisons. Furthermore, the reference material prepared by BAM, that simulates the gas emission behaviour typical of 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. Another interlaboratory comparison, organised by NPL, for the analysis of components in indoor air included 23 participants; they included European institutions, analytical labs and end users including indoor air quality testing labs, emission testing labs and chemical producers.

Significant attention has been paid to the project's research on zero gas standards. The MACPoll workshop on zero gases, organised in June 2013, has 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 has also been implemented in the certification of nitrogen and air zero gases prepared by Linde a gas specialty producer.

In addition to this, 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). The assessment results on the performance of a selection of micro-sensors for the measurement of specific air pollutants (NO_2 and ozone) are also particularly beneficial for sensors manufacturers, as these results are helping them build more reliable and accurate devices. The direct beneficiaries are the manufacturers which have provided the sensors for testing, such as AlphaSense and Cairpol.

Finally, air monitoring networks and environmental authorities have benefitted from the project's results on gas sensors, as they give guidance on the state-of-the-art in gas sensing and help end-users to understand the pros and cons of these sensor devices when applied in the field. In the longer term, this will have an impact on the implementation of the EU Air Quality Directive (2008/50/EC) and in particular on the use of indicative methods for ambient air monitoring.

4.3.3   Scientific uptake

All results from the MACPoll project have been disseminated and well received by the scientific community. The publication on the adsorption effect of trace concentrations of NH3 gas on contact materials based on the work performed by the EMRP researcher at the University of Helsinki has been used as an example and

literature reference. Furthermore, SilcoTek, an expert company in inert coating and a project collaborator made use of the project results in their scientific and marketing presentations.

Within EURAMET a new comparison (EURAMET 1329) is in the process of being organised to establish the comparability of SO_2 calibration gases for reactive pollutants. This comparison, which is open to European NMIs, is a follow-up of the MACPoll comparison on reactive gases and it will allow the scientific knowledge gained in the project to be used and shared within Europe.

As often happens in scientific research, MACPoll results have also demonstrated that there is a need for further research in metrology for air quality, and follow-on EMRP projects, MetNH3 (Metrology for ammonia in ambient air) and KEY-VOCs (Metrology for VOC indicators for air pollution and climate change) have been funded as part of the EMRP Call 2013 Environment.

4.4   Longer-term impact

Standardisation and metrological activities are fundamental for the establishment of a proper measurement infrastructure in air quality. In the longer term, it is expected that the certification protocol for zero gases and the evaluation protocol of micro-sensors for air monitoring (both produced by this project) will feed into the preparation or revision of documentary standards in European and International technical committees dealing with gas analysis and air quality.

The provision of metrological traceability, through the correct use of reference standards and methods developed in this project, should also lead to the improvement of the current measurement techniques for air monitoring. Better comparability and harmonisation of measurement data throughout Europe should lead to compliance with environmental legislation and therefore to a better understanding of the trends in air quality.

The project's metrological outputs for (S)VOC should also strongly impact emission labelling schemes, responsible for the detection of hazardous compounds emitted by building materials. By improving the quality of these schemes, the Construction Products Regulation can be better enforced and hence the risk of indoor pollutants in buildings will be reduced.

The urgent need for a proper validation protocol for gas sensing devices to confirm their reliability for use in air monitoring networks and no less important, the need to demonstrate the metrological traceability of their measurements results have been major drivers in the MACPoll project. The project's outcomes therefore represent an important step towards the set-up of a new measurement infrastructure for air monitoring. In the near future, when gas sensor performances are successfully demonstrated, the devices will represent a new way to perform air monitoring, because they could be used as indicative methods, allowed by the Air Quality Directive, with the additional advantages of being low-cost, providing real-time data and a large space coverage.

5   Website address and contact details

Project website address www.macpoll.eu

After registration, the download area of the website becomes accessible and important public project outputs are freely available.

Contact details

For further information on the project, contact Mrs. Annarita Baldan, VSL (ABaldan@vsl.nl).

For information on calibration gases for existing EU Air Quality Directive pollutants at limit values, contact Mrs. Tatiana Macé, LNE (Tatiana.Mace@lne.fr).

For information on Zero Gas Standards, contact Mr. Stefan Persijn, VSL (SPersijn@vsl.nl).

For information on traceability for the measurement of (S)VOC in indoor air and constant emitting materials for quality assurance purposes, contact Mr. Matthias Richter, BAM, (matthias.richter@bam.de).

For information on micro-sensors for air quality measurements, contact Mr. Michel Gerboles (michel.gerboles@jrc.ec.europa.eu).

6   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)