



# Current & Future Air Quality Monitoring

# Workshop and Conference with Posters and Exhibition

Jointly organised by the Automation and Analytical Management Group -Royal Society of Chemistry and AirMonTech

#### Tuesday 14th & Wednesday 15th December 2010

At The Royal Society of Chemistry, Burlington House, Piccadilly, London W1J 0BA

Email: conference@aamg-rsc.org Website: http://www.aamg-rsc.org

RSC Advancing the Chemical Sciences

## **Current & Future Air Quality Monitoring**

Workshop & Conference with Exhibition

Tuesday 14<sup>th</sup> & Wednesday 15<sup>th</sup> December 2010 at The Royal Society of Chemistry, Burlington House, London

## Day 1 - Tuesday, 14<sup>th</sup> December 2010

09:00 Registration

## Measurement Technologies for Regulated Compounds in Air Quality Assessment

- 10:00 *Welcome Address*  **Paul Quincey** National Physical Laboratory, UK
- 10:10 *Introduction to AirMonTech* **Thomas Kuhlbusch** IUTA e.V., Germany
- 10:30 *Outline of WP1* Christoph Hueglin E M P A, Switzerland
- 10:50 Tea / Coffee Exhibition & Posters

## **Existing Technologies for Regulated Metrics**

Chairperson: Annette Borowiak, European Commission DG - JRC, Italy

- 11:10 *Principles of Type Approval for Monitoring Systems*  **Peter Woods** National Physical Laboratory, UK
- 11:30 *Equivalence Tests: Principles and the PM Issue* Ulrich Pfeffer LANUV NRW, Germany
- 11:50 Ongoing QA/QC for PM Monitoring: Requirements from AMS Group of TC264/WG15 Theo Hafkenscheid R I V M, The Netherlands
- 12:10 Lunch Exhibition & Posters

- 13:20 Developments and Recommendations for EC/OC Monitoring Jean-Philippe Putaud European Commission DG - JRC, Italy
- 13:40 NO<sub>2</sub> Measurements with Different Converters; Molybdenum Converters vs. Specific NO<sub>2</sub> Converters Robert Gehrig E M P A, Switzerland
- 14:00 Analytical Characteristics for Benzene (and VOC) Automatic Measuring System: Results From Laboratory Tests and Field Campaign Nadine Locoge Ecole des Mines de Douai, France
- 14:20 *General Discussion : How to Proceed in WP1* Existing type approvals, SOP and equivalence reports: what exists, what is missing where available. How to collect the information. How to assess and disseminate the information.
- 15:10 Tea / Coffee Exhibition & Posters

## Data Collection and Dissemination Within AirMonTech

Chairperson: Rene Otjes, E C N, The Netherlands

15:40 WP 3: The AirMonTech Database Annette Borowiak European Commission DG - JRC, Italy

## New Technologies for Regulated Metrics

- 16:20 Sensors for Monitoring Regulated Compounds Michel Gerboles European Commission DG - JRC, Italy
- 16:40 *Mobile Multi-Species Trace Vapour Sensors for Localized Pollution Monitoring and Mapping* Mark Richards Imperial College London, UK
- 17:00 Performance of Laser Spectroscopic Techniques for the Determination of Regulated Compounds Christoph Hueglin E M P A, Switzerland
- 17:20 Discussion on New Technologies for Regulated Metrics
- 17:30 End of Day One

## Day 2 - Wednesday, 15<sup>th</sup> December 2010

# New Metrics, Technologies and Strategies in Air Quality Monitoring

09:00 Introduction Day 2 Ulrich Quass IUTA e.V., Germany

## **New Technologies and Alternative Metrics**

Chairperson: Mar Viana, C S I C, Spain

- 09:10 *Knowns, Unknowns and Needs for Health Relevant New Metrics* Klea Katsouyanni University of Athens Medical School, Greece
- 09:30 **ROS A Potentially Health Relevant Alternative Metric Frank Kelly** King's College London, UK
- 09:50 Particle Surface Area Measurements Are Current Techniques Applicable? Thomas Kuhlbusch IUTA e.V., Germany
- 10:10 Tea / Coffee Exhibition & Posters
- 10:40 *New Potentiometric Method for Automatic Detection of Bioaerosols Dimitris Sarantaridis* University College London, UK
- 11:00 Instrumentation Based on Wet Sampling Techniques with On-Line Detection
   Rene Otjes
   E C N, The Netherlands
- 11:20 Source Contribution An Alternative Metrics Xavier Querol C S I C, Spain
- 11:40 Discussion on New Technologies and Alternative Metrics
- 12:20 Lunch Exhibition & Posters

## **New Monitoring Strategies - Approaches**

Chairman: Paul Quincey, National Physical Laboratory, UK

- 13:20 Application and Limitations of Satellite Remote Sensing Technology for Estimating Air Emissions and Concentrations of Pollution at Ground Level in Low-Latitude Climates Mofoluso Fagbeja University of the West of England, UK
- 13:40 The German Ultrafine Aerosol Network Experience with Routine Particle Size Distribution Measurement Wolfram Birmili i f T, Germany
- 14:00 UK Particle Number Measurement Network Paul Quincey National Physical Laboratory, UK
- 14:20 *Personal Monitoring of Exposure to Black Carbon* Evi Dons V I T O, Belgium
- 14:40 Development of a New Measuring Bike for Mapping Dust Levels in Urban Environments: The Aeroflex Bike Martine Van Poppel VITO, Belgium
- 15:00 Discussion on Metrics and Monitoring Strategies Related to Health Effects
- 15:30 Tea / Coffee Exhibition & Posters

# What is Needed to Evaluate/Establish New Technologies and New Metrics?

Chairperson: Annette Borowiak, European Commission DG - JRC, Italy

- 16:00 *Future Urban AQ Monitoring in Europe* Emile De Saeger European Commission DG - ENV, Belgium
- 16:20 How Can Background Measurements Be Linked with Urban Air Quality Monitoring Kjetil Tørseth N I L U, The Netherlands
- 16:40 *Wrap-up and Outlook* Thomas Kulhbusch IUTA e.V., Germany
- 17:00 End of Conference

# ABSTRACTS

## **Outline Of WP1: Recent Technologies For Air Pollution Monitoring**

Christoph Hueglin<sup>a</sup>, Annette Borowiak<sup>b</sup>

<sup>a</sup> Empa, Materials Science and Technology, Duebendorf, Switzerland <sup>b</sup> Joint Research Centre (JRC), Institute for Environment and Sustainability, Ispra, Italy

#### ABSTRACT

Innovation in air pollution monitoring is of vital importance to cope with the growing needs for new metrics and high data availability, which leads to an increasing number and complexity of available instruments. In the short term, harmonisation is needed to ensure comparability of measured concentrations and associated measurement uncertainties provided by European air pollution monitoring networks.

One of the objectives of AirMonTech is to support harmonisation of air pollution monitoring by providing required information, recommendations and guidance for operation of available measurement technologies. The focus of Work Package 1 (WP1) within the FP 7 AirMonTech project is on currently used in-situ monitoring technologies for air pollutants regulated in Directive 2008/50/EC, namely the inorganic gaseous pollutants SO<sub>2</sub>, CO, NO/NO<sub>2</sub>, O<sub>3</sub> and benzene, as well as the particulate matter fractions PM10 and PM2.5.

WP1 feeds into a database, which will be created within AirMonTech, containing information on instruments and their type approval tests carried out in the different Member States and the USA. Currently the type approvals are mostly valid in one Member State or one pollution region only. Guidance will be developed to promote intra-European data exchange and the use of National type approvals for other Member States and pollution areas as well.

Another main task of WP1 is to provide guidance on operation, maintenance and calibration of air quality monitoring instrumentation. A database on standard operating procedures (SOPs) will collect and evaluate documents of European air quality monitoring networks on set-up, operation, maintenance, calibration and quality assurance for available automated instruments for gaseous and particulate air pollutants.

Finally, access to equivalence tests between reference and candidate methods will be provided by WP1. The problem of equivalence occurs mainly for particulate matter. A collection of data on performed PM equivalence testing is crucial for an efficient use of resources in Europe. Many networks have carried out field tests and trials to test the equivalence of instrumentation to measure particulate matter in comparison to the reference methods EN 12341 and 14907. Available information and data on PM and possibly other background information (e.g. meteorology) will be collected and compiled, so that users will be able to use the data for their specific needs.

## Type-approval of Ambient Air Measurement Methods to Provide Conformance with EU Directives and CEN Standards

#### Peter T Woods

National Physical Laboratory, Hampton Rd, Teddington, TW110LW, UK

#### ABSTRACT

The recently published European Directive entitled "Directive 2008/50/EC on ambient air quality and cleaner air for Europe" replaced a number of previous ambient air directives, and it sets up the required infrastructure for the use of published CEN standards for monitoring the regulated ambient air pollutants. This Directive, now enacted into UK legislation, defines a number of monitoring requirements including:

- Limit values for the concentration levels of pollutants that should not be exceeded;
- The measurement uncertainties that all the measurement results must conform to if these are to be reported to the Commission for demonstrating a Member State's compliance with the EC's requirements.

The Directive also defines (Annex VI) a range of CEN standards that are to be used as "reference measurement methods" for the monitoring of all these air pollutants. Certain of these CEN reference methods (for  $SO_2$ ,  $NO_x$ , CO,  $O_3$ , and benzene) cover continuous automated instruments. These were mandated by the Commission (before the standards were being drafted) to be type approved before use to ensure that they comply with the Directive's measurement uncertainty requirements.

These continuous reference methods are different from other reference methods given in the directive – e.g. for particulates and their speciation - where manual reference methods are specified, and there is a requirement to demonstrate the "equivalence" of any other automated or manual method that is used.

This presentation discusses the requirements for the type approval of these continuous reference methods, discusses how these type approval tests must be carried out, and outlines the ongoing quality assurance and quality control methodologies that must be adopted to ensure that the methods continue to provide results in the field with the required measurement uncertainties and other characteristics. The testing that would be required for methods other than these continuous reference methods will also be outlined.

There is a requirement that the tests specified in the CEN standards are carried out under the framework of a valid relevant accreditation to the EN ISO 17025 standard and this will be outlined. There are currently also on-going discussions on the mutual acceptability of these type-approval testing results in different Member States of the EU, in different fora, particularly that of the AQUILA Group of "National Reference Laboratories", and the current status of these discussions will be summarized.

## **Equivalence Tests: Principles And The Pm Issue**

Ulrich Pfeffer, Jutta Geiger, Thorsten Zang Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen (LANUV NRW) Wallneyer Straße 6, D- 45133 Essen (Germany), ulrich.pfeffer@lanuv.nrw.de

#### ABSTRACT

Ambient measurements of particles, e. g.  $PM_{10}$  or  $PM_{2.5}$ , are different from the measurement of gases because of the lack of full traceability. Therefore, these measurements have to be performed based on standard methods as described in European standards like EN 12341 ( $PM_{10}$ ) or EN 14907 ( $PM_{2.5}$ ). The standards mentioned were defined as reference methods in 'DIRECTIVE 2008/50/EC OF THE PARLIAMENT AND OF THE COUNCIL of 21 May 2008 on ambient air quality and cleaner air for Europe'. This directive also includes so-called Data Quality Objectives (DQO), especially the maximum expanded uncertainties of single measurement values.

For various reasons, PM measurements are in practise often performed with automated monitoring systems (AMS). According to the Directive mentioned above, for these non-reference methods equivalence to the reference method has to be demonstrated.

The principles of demonstrating equivalence and examples of equivalence trials especially for automated monitoring instruments will be given showing that severe problems with various instrumentations may occur and are difficult to detect.

LANUV as National Reference Laboratory for Germany (GeRLAP) also organized field inter-comparisons for the German networks. After a big campaign for  $PM_{10}$  in 2003 a similar field comparison for  $PM_{2.5}$  was performed in 2008/2009. Results show that the DQO set by the EU Directive can safely be met for gravimetric instruments. For automated instruments this is not always the case.

Because equivalence tests are performed by many institutes across Europe a validated data base with all these results would be extremely helpful.

#### References

DIRECTIVE 2008/50/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 May 2008 on ambient air quality and cleaner air for Europe, Official Journal of the European Union, 11.06.2008, L 152/1-44

Ulrich Pfeffer, Thorsten Zang, Reinhold Beier, Eva-Maria Doutnik: Experiences with Equivalence Testing in Germany, Proceedings of the Workshop on Demonstration of Equivalence, 2-4 May 2007, Ispra (Italy) JRC Scientific and Technical Reports, EUR 23216 EN – 2008, pp. 21-22, pp. 54-60

## **Ongoing QA/QC for PM Monitoring**

## Requirements from AMS Group of TC264/WG15

**Theo Hafkenscheid** RIVM Centre for Environmental Monitoring NL – Bilthoven

### ABSTRACT

CEN/TC264 "Air Quality" Working Group 15 is currently drafting a standard for the application of automated continuous measurement systems (AMS) for particulate matter (PM). Elements of this standard are:

- Demonstration of equivalence by
  - Type approval of an AMS
  - o Suitability evaluation of an AMS for application in a particular network
- Ongoing QA/QC of measurements
- Data treatment.

The procedures for ongoing QA/QC aim at:

- Checking that each individual AMS operates within pre-specified performance requirements
- Checking that the claim to equivalence of the AMS is maintained.

The latter purpose is realized through performance of ongoing parallel measurements with the reference method and evaluation by comparison of the measurement results of both methods.

This presentation will provide information on the new draft standard in general and on the principles and procedures foreseen for ongoing QA/QC.

## Developments And Recommendations For Monitoring Atmospheric Particulate Organic And Elemental Carbon

Jean-Philippe Putaud European Commission, Joint Research Centre, Institute for Environment and Sustainability, I-21027 Ispra (VA)

#### ABSTRACT

The European Directive on ambient air quality 2008/50/EC (21 May 2008) states that measurements shall be made at rural background locations for providing information on the chemical speciation of fine particulate matter ( $PM_{2.5}$ ). This includes the determination of organic carbon (OC) and elemental carbon (EC) concentrations, which is not trivial since (1) particulate OC sampling can be affected by artifacts, and (2) no scientific distinction can be made between OC and EC, while carbonate (CC) can interfere with both. Recent developments occurred in both the technical and standardization fields.

A great deal of research was performed in the framework of the EU-funded FP6 project EUSAAR. Tests performed at 7 regional background sites across Europe showed that quartz filter sampling is affected by a positive artifact equal to 14 - 70% (site dependent). Positive artifacts can be efficiently reduced thanks to commercially available denuders, while negative artifacts are not significantly increased according to current knowledge. However, the reference method for sampling PM<sub>2.5</sub> (EN 14907:2005) does not include the use of denuders. EUSAAR also showed that the most commonly used thermal protocols for determining OC and EC (IMPROVE, NIOSH5040, and NIOSH-like methods) are affected by significant biases, which are minimized by the newly developed EUSAAR2 protocol, tested against numerous synthetic and natural samples. Furthermore, the temperature plateaus during which CC evolves were well proven, and a simple, independent method for determining CC was proposed.

Regarding standardization, the European Committee for Standardization – Technical Committee for Air Quality (CEN – TC 264) recently released its "Guide for the measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters". It describes several protocols for thermal-optical methods that will give different results for OC and EC, until one standard method is specified, based on results of validation tests. EMEP (the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe) will also update its "manual for sampling and analysis" shortly. EMEP recommendations and standard methods should be compatible.

## NO<sub>2</sub> Measurements with Different Converters; Molybdenum Converters vs. Specific NO<sub>2</sub> Converters

*Robert Gehrig,* Christoph Hüglin, Beat Schwarzenbach Empa Materials Science and Technology, Air Pollutants/Environmental Technology, Dübendorf, Switzerland

#### ABSTRACT

Measurements of nitrogen dioxide (NO<sub>2</sub>) for compliance monitoring are usually performed with chemiluminescence analyzers using molybdenum converters. This is generally accepted though it is well known that molybdenum converters do allow for a specific measurement of NO<sub>2</sub> as they not only reduce NO<sub>2</sub> to NO but in addition a couple of other oxidized nitrogen compounds like nitric acid, nitrous acid, nitrates and PAN. Specific NO<sub>2</sub> measurements can be obtained with chemiluminescence instruments using photolytic converters reducing NO<sub>2</sub> specifically by irradiation with UV light below 410 nm. These devices are increasingly used in cases where specific information on NO<sub>2</sub> is required. The differences between unspecific and specific NO<sub>2</sub> measurements can be quite considerable.

Long-term data from parallel measurements comparing NO<sub>2</sub> data obtained with molybdenum converters with specific NO<sub>2</sub> data obtained with photolytic converters at different sites in Switzerland reveal the significant differences between these methods. The absolute concentration differences  $\Delta NO_2$  [ $\Delta NO_2 = NO_2$  (molybdenum) – NO<sub>2</sub> (photolytic)] were in the range of 1.7 – 2.2 ppb, showing only moderate variability from site to site. At rural sites this corresponds to a 25 – 50% overestimation of NO<sub>2</sub> measured with non-specific molybdenum converters. At more polluted urban sites the overestimation is still around 12%. For single daily values the differences can be even much larger.

EN 14'211 defining the reference method for NOx measurements is not explicitly addressing this issue. The standard is just requiring a minimum conversion rate of the converters and limiting the interference to NH<sub>3</sub>, but not to the strongly interfering oxidized nitrogen compounds mentioned above.

Because nearly all  $NO_2$  data series were until recently based on measurements with molybdenum converters the comparability was not seriously hampered. However, as photolytic converters as well as new specific spectroscopic techniques are more and more available and employed, this is likely to change in near future. In order to correctly deal with  $NO_2$  data it becomes therefore important to provide proper information about the used measurement method with all  $NO_2$  data.

## Analytical Characteristics For Benzene (And VOC) Automatic Measuring System: Results From Laboratory Tests And Field Campaign

Nadine Locoge<sup>1,2</sup>, Thierry Léonardis<sup>1,2</sup>, François Mathé<sup>1,2</sup>
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 (2) Ecole des Mines de Douai, Département Chimie et environnement, F-59508 Douai, France

As required by the directive 2008/50/EC, the reference method for sampling and measurement of benzene is the pumped sampling method on a sorbent cartridge followed by gas chromatography determination as described in EN 14662 (part 1, 2 and 3): 2005. In France, two methods are commonly used: Automated Measuring System (AMS, automatic analysers) since more than 10 years, and more recently, active samplers under specific validated conditions (sampling duration of 7 days at a flow rate of 10mL.min<sup>-1</sup>) [1,2].

Besides fixed measurements are complemented with passive samplers. Usually, the automatic instruments were used as reference method for comparison with the other methods. But differences have been observed and in some cases a relatively poor agreement was found between active samplers and automatic analysers. A question was consequently raised: "Are all the automatic instruments (different models from different manufacturers) used in French AQ networks comparable if they are used simultaneously in field campaigns?"

The objective of this study is to compare results obtained in terms of VOC (Benzene, Toluene and Xylenes) concentrations measured with automatic analysers. These instruments were used in the same QA/QC conditions as in the networks: "single point" calibration, calibration check every 14 days, flow control...

The 5 automatic instruments tested in this study corresponded to the analyzers used in the French networks (VOC 71M-FID from Environnement SA, VOC 71M-PID from Environnement SA, AirmoBTX-FID from Chromatotec, GC 955-PID from Synspec, TurboMatrix TD/Autosystem-FID from Perkin Elmer developed for the continuous monitoring of 56 hydrocarbons (C2 to C9) [3].

The study was organized in two parts:

✓ Individual metrological validation of each instrument for several performance characteristics (in the laboratory), before installation in the field. These laboratory tests consisted in repeatability at  $0.5\mu g/m^3$  and at  $5\mu g/m^3$ , memory effect and detection limit; the analysers fulfilled these performance criteria of EN standard. But one system failed on lack of fit test and two monitors showed interference problem from sum of possible interfering organic compounds at span value (for one analyser, the interference was linked to isooctane, not included in the possible interfering compounds but highlighted from results of field campaign).

After the validation lab tests, field campaign of 5 weeks (from  $11^{th}$  may to  $2^{nd}$  june 2007) in a monitoring station (high traffic-oriented site) in order to evaluate the parallel measurements of BTX concentrations. A particular attention was brought to C<sub>6</sub>H<sub>6</sub> measurements (the only compound under regulation). The daily variations of VOC concentrations were studied by comparing the values obtained with the 5 monitors. For all the target compounds, the 5 automatic analysers gave daily evolutions which were globally consistent with a diurnal bimodal frequency

distribution of the concentrations. This proves the important contribution of the traffic density to the measured concentrations. Nevertheless, for benzene, some important differences in the measured concentrations were observed depending on the analyser. There was a relatively good agreement between 3 automatic systems (VOC 71M-PID, AirmoBTX-FID and TurboMatrix ATD-FID). A significant underestimation was observed with GC 955 Synspec-PID (the only AMS to be type-approved [4]) and VOC 71M-FID gave a significant overestimation. To highlight these "differences", the mean concentration over all the campaign measured by the 5 automatic systems varied from  $0.9\mu$ g/m<sup>3</sup> to  $3.2\mu$ g/m<sup>3</sup>. For simultaneous hourly measurements, this range reached 3,1 to  $11.6\mu$ g/m<sup>3</sup>. It should be stressed that all the analysers were calibrated with the same gas mixture, connected to the same sampling manifold and controlled by the same operator for QA/QC procedures.

From this study, it was clearly identified that benzene mean level depends on the automatic analyser used and may vary in a large scale (more than 3 times higher from a system to another one). As a consequence, it can be assumed that at some sampling sites, the benzene averaged value measured during a campaign exceeds or not the Upper Assessment Threshold (UAT) set by Directive 2008/50/EC. So depending on the system used for assessment, the required measurement strategy may be completely different, from implementation of fixed measurements ([ $C_6H_6$ ] > 3,5µg/m<sup>3</sup>) to use of objective estimation ([ $C_6H_6$ ] < 2µg/m<sup>3</sup>). The requirement of type-approved analysers is one of the key points for quality assurance of "true" benzene measurements and forthcoming revision of EN 14662-3 could include additional tests such as field campaign with different models of type-approved monitors put in parallel.

#### References :

[1] N.Locoge, H.Plaisance et I;Chiappini, Rapport 2008. Surveillance du benzène 3/5 : Surveillance du benzène par la méthode d'échantillonnage actif, application de la norme 14662-1. Etude LCSQA-EMD-INERIS, 2008 – disponible sur

http://www.lcsqa.org/rapport/2008/ineris-Ine-emd/surveillance-benzene

[2] N.Locoge et L.Chiappini, Rapport 2009-2. Surveillance du benzène 2/2 : la méthode de référence (échantillonnage actif). Etude LCSQA-EMD-INERIS, 2009 – disponible sur <u>http://www.lcsqa.org/rapport/2009/emd-ineris/surveillance-benzene-22-methode-reference-echantillonnage-actif</u>

[3] N.Locoge, T.Léonardis, Rapport 2007. Mesure du benzène 3/3 : Tests d'évaluation des analyseurs automatiques de BTEX. Etude LCSQA-EMD, 2007 – disponible sur : http://www.lcsqa.org/rapport/2007/emd-ineris/mesure-benzene

[4] « Supplementary report to the type-approval-test of gas chromatograph GC 955 Serie 601 of Synspecc » - UMEG Report n°53-09/05 (26.04.06)

## WP 3: The Airmontech Database

*Annette Borowiak*<sup>a</sup>, Luca Maria Ernesto Spano<sup>b</sup> <sup>a</sup> Joint Research Centre (JRC), Institute for Environment and Sustainability, Ispra, Italy <sup>b</sup> Reggiani Spa, Gavirate, Italy

#### ABSTRACT

The FP 7 AirMonTech project aims at improving the use, data quality and comparability of air pollution measurements. For that purpose a database will be created, which stores the most important information regarding the measurement technologies of air quality.

A web application will be built on top of the database and it will allow users to interact with the data store. It is planned that the system is designed under the .NET Framework and it mainly relies on the following technologies: ASP.NET (user interface), IIS (application server) and SQL Server (database).The user interface allows to subscribe and log into the system, search contents, upload and download files.

The authentication is based on email address and password provided by the user through a login form. New subscriptions must be confirmed and requires new users to undergo an email verification process before their account is activated..

Three different roles will be defined and managed by the system: system administrator (managing users and technical details), editor (uploading and flagging files), standard user (search and download).Users who do not subscribe to the system (guests) can still surf the website but have no rights to download files). Proposed search engine and options are a basic full text search and an advanced search with predetermined filters.

The structure and information foreseen to be included into the database contains: air pollutants (and further general information on the pollutant), metrics of the pollutant (e.g. TSP, PM10 or particle number concentration), measurement techniques related to the metrics, instruments/technologies available to measure the metrics and finally operation procedures for the different technologies and equivalence/type approval tests where available. The information flow, inputs and outputs of the database will be discussed with the air quality monitoring community in project workshops and at AQUILA meetings.

## **Sensors for Monitoring Regulated Compounds**

Michel Gerboles,

Joint Research Centre, Institute for Environment and Sustainability, Transport and Air Quality Unit, Via E. Fermi, I – 21027 Ispra (VA)

#### ABSTRACT

The European Air Quality Directives implies the monitoring of ambient air for NO<sub>2</sub>/NOx, SO<sub>2</sub>, O<sub>3</sub>, CO, benzene, PM against limit and target values. Reference methods of the highest metrological quality with low measurements uncertainty are defined in the Directives for the ambient air monitoring. These reference methods are expensive and require continuous site maintenance, calibration and electric supply. However, the Directives allow using indicative methods having a higher measurement uncertainty than the reference methods.

Recent technological progress has made available a wide family of cheaper and smaller sensors that allow the monitoring of gaseous compounds or particulate matter. Sensors have a good potential to reach the status of indicative methods. They have additional abilities either for fixed or mobile monitoring of human exposures and for mapping spatial distribution of pollutants. Recent studies mainly emphasize the development of new highly sensitive sensors or appealing Web reporting services that combine the potential of sensors with GPS/GSM possibilities. Unfortunately, the validation of the metrological performances of sensors is mainly disregarded. As a result of this lack of validation data, there is a hesitancy to apply these sensors for monitoring regulated compounds.

Different types of sensors suitable for which validation data in relation with the data quality objectives of the European Directive are available will be presented. In the absence of an official validation protocol, some examples of key parameters to be assessed for validation purposes (e. g. response time, warming time, linearity, drift, matrix effects, meteorological conditions and interferences) will be given. Some strategies for laboratory of field calibration of sensors will be suggested and a direction for future validation programs will be given.

## Mobile Multi-Species Trace Vapour Sensors For Localised Pollution Monitoring And Mapping.

*Mark Richards\*,* Steven Wilkins\*\*, and John Hassard\* \* Department of Physics, Imperial College London, UK \*\*Duvas Technologies Ltd, UK

#### ABSTRACT

In this paper we describe recent developments in high throughput multi-species (Duvas) sensors that can rapidly identify, monitor and map air pollution within an urban environment on a street-by-street basis. As a result, it is now possible to dynamically retrieve time-critical data on a large scale through a combination of Furthermore, advances in network static, portable, and mobile air sensing. architecture, communications devices, and grid computing now enable the gathering, integration, analysis, and visualization of pollution data within a wireless sensor network environment. Additionally, the implications for real-time decision-making and the effectiveness of reducing the likely impact of local air quality are also discussed. Finally we expand further to demonstrate how the progression from a real-time sensor grid towards an early warning and forecasting system could be achieved through intelligent data warehousing and analytical workflows. The outputs of this work have global reach and are pertinent throughout the developed and developing world alike as there are many densely populated areas within these regions that must strike a balance between sustainable economic growth and an overall reduction in the environmental impact of emissions on climate and health. The sensing technologies developed herein could facilitate a significant shift towards evidencebased decision making.

## Performance Of Laser Spectroscopic Techniques For The Determination Of Regulated Compounds

#### Christoph Hueglin

Empa, Materials Science and Technology, Duebendorf, Switzerland

#### ABSTRACT

During the past few years, new analytical techniques for automated measurements of air pollutants have been developed, and new generations of instruments have become available on the market. Novel instruments based on laser spectroscopic techniques are examples of a new generation of instruments that are already commercially available for in-situ measurements of atmospheric trace gases, including regulated compounds, such as NO<sub>2</sub> and CO. Analyzers for other air pollutants relevant for urban air quality will very likely become available in the near future. These instruments offer the possibility of highly sensitive and accurate measurements with high precision and temporal resolution.

Within AirMonTech, the applicability and performance characteristics of new online measurement technologies for air pollution monitoring will be evaluated. This assessment will cover important issues such as comparability to (manual) reference methods, detection limits, selectivity, measurement uncertainty, calibration procedures, suitability for use in air quality monitoring networks, and operation costs.

The Air Pollution and Environmental Technology Laboratory at Empa has strong experience in the development and application of laser spectroscopic techniques for the measurement of atmospheric trace gases. In this presentation, a brief introduction into these novel measurement techniques (e.g. quantum cascade laser absorption spectrometry, QCLAS, and cavity ringdown spectroscopy, CRDS) will be given, and their potential for air quality monitoring will be discussed.

## Knowns, Unknowns And Needs For Health Relevant New Metrics

#### Klea Katsouyanni

Department of Hygiene, Epidemiology and Medical Statistics University of Athens Medical School

#### ABSTRACT

The last two decades have seen a dramatic change in our knowledge about the health effects of air pollution. There is today a wide consensus that exposure to air pollutants (mainly particulate but also gaseous) has important effects on health and that there is no safe level. It is also known that not all population subgroups are affected in the same way, there are sensitive subgroups such as the elderly and those with chronic illness. It is true that although some biologic mechanisms to explain the effects of particulate pollution have been suggested and some have been verified, it is not clear yet which of the physical and chemical characteristics of particles are responsible for each specific health outcome.

However, air pollution abatement strategies face difficulties since the composition of particulate pollution depends on the source, climate, topography and meteorology and it is not clear which components are the most important for the protection of public health.

Within the framework of AirMonTech, a systematic approach will be taken to standardize and establish monitoring strategies which will allow a better understanding of the characteristics of particulate pollution in relation to population exposure and health. The link with health effects is an important issue for informed decisions about which items or mixtures to monitor.

In this presentation we will review the knowledge about the effects of particles from specific sources or those with specific characteristics. Thus, there is evidence that the size of particles is important and exposure eg to coarse or ultrafine particles is associated with different health outcomes. The number of particles (in contrast with mass which is the regulated metric to date) appears to be important. On the other hand several chemical characteristics of particles have been implicated, for example sulfates, nitrates, organic carbon and transition metals. Another health relevant classification is between primary (emitted) and secondary (formed in the atmosphere) particles which have been associated with different outcomes as well.

Additionally there are several studies implicating particles from traffic as responsible for the severity of effects and indications that these particles are more toxic compared to particles from other sources. Recently studies of particles from other origins such as desert dust transported over long ranges and particles from bush or forest fires are being reported with inconclusive findings.

In conclusion, AirMonTech will aim at reaching a coherent proposal for future measurement metrics and strategies allowing a stronger link between online measurements, population exposure and, hence, the better understanding of health effects.

## **ROS – A Potentially Health Relevant Alternative Metric**

### F.J. Kelly

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#### ABSTRACT

Appreciation of the adverse health effects of PM from epidemiologic and controlled exposure studies has led to the establishment of mass-based air quality standards for particles according to particle size. It is however widely accepted that PM mass represents only a surrogate of the biologically active dose of particles, and is therefore far from an ideal metric (Kelly, 2003). PM is a complex mixture, and there is considerable interest in the specific components responsible for the observed health effects (Borm et al, 2007). Clearly a better understanding of the properties or components of PM that are most linked with health effects will allow for the development of more targeted and efficient control strategies (Defra, 2007a).

The mechanisms underlying PM related health effects are still incompletely understood. One popular hypothesis under investigation is that many of the adverse effects may derive from PM induced formation of reactive oxygen species (ROS) at the surface of and within, target cells. There is a growing literature on specific health effects in association with cellular oxidative stress, including the ability of PM to induce pro-inflammatory effects in the nose, lung and cardiovascular system. Consequently, tests designed to quantify the potential of particles to exert oxidative stress have been developed, and are being used in a comparative manner to evaluate those particle properties, most influential in eliciting toxicity.

At King's College London we have established an *in vitro* screening system, which involves the incubation of PM samples within a synthetic respiratory tract lining fluid (Zielinski et al., 1999; Mudway et al., 2004). The respiratory tract lining fluid (RTLF), represents the first physical interface encountered by inhaled materials and contains high concentrations of the antioxidants ascorbate (vitamin C), urate and reduced glutathione (GSH). Examining the extent to which PM depletes antioxidants from this model with time (37°C, pH7.4) thus provides not only a quantitative output of activity, but also reflects reactions likely to occur *in vivo* at the air-lung interface. My presentation will provide an overview of progress with this approach and other developments by other research groups in this area.

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#### Particle Surface Area Measurements -Are Current Techniques Applicable?

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#### ABSTRACT

Particle metrics currently discussed to be of possible health relevance are particle number and surface area concentrations besides mass. The particle surface area is the interface between the particle and the biological fluids and toxicological effects of TiO<sub>2</sub>-particles have shown to correlate best with their total surface area (Oberdörster et al., 2000). Moreover, epidemiologic studies show an increased risk for cardiovascular health problems with shorter distance of residence to major roads (B. Hoffmann et al, 2007) indicating potential relevance of submicron and ultrafine particles.

So far no long-term data on atmospheric particle surface area concentration have been reported to our knowledge. Therefore, particle surface area measurements were conducted at an urban background site in Mülheim-Styrum in the Ruhr-Area, Germany starting March 2009. More specific, the lung deposited particle surface area concentrations were measured with a Nanoparticle Surface Area Monitor (NSAM, TSI 3550) and were calculated from simultaneously measured particle number size distributions, based on the assumption of spherical particles.

Fig. 1 depicts the correlation of the measured to calculated surface area concentrations (based on total-range SMPS-data) as well as that to ultrafine particle (UFP) number concentrations derived with an SMPS. Fig. 1 clearly shows the good correlation between the calculated (for total SMPS range) and measured surface area concentrations with a slope close to one.

From Fig. 1 it is also evident that no correlation exists between UFP number and lung deposited particle surface area concentrations for 30 min. averages. Hence both concentrations can be viewed as being independent from each other and can be used as independent exposure metrics.

The quality assessment of the measurement technique and data presented here on particle surface area concentrations at an urban background site for the first time show the feasibility for ambient air quality monitoring. It could also be shown that surface area concentrations can be viewed to be an independent metric. Hence its use in exposure assessment and concurrent epidemiological studies should be tested. Furthermore the influence of humidity on particle surface area measurements was also investigated as a quality assurance measure.



Fig. 1: Correlation of measured and calculated particle surface area and measured UFP number concentrations (30 min. values, 1.3.-30.6.2009)

Results from the atmospheric comparison measurements and the QA/QC-study will be presented.

We like to acknowledge the MUNLV of NRW for sponsoring part of this work. Thanks are extended to U. Pfeffer and P. Bruckmann for their support.

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## A New Potentiometric Method For Automatic Detection Of Bioaerosols

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#### ABSTRACT

Detection of bioaerosols is important for many applications including climate, wellbeing and security. Current methods for unambiguous identification of airborne bacteria, spores and viruses rely generally on either expensive methodology, such as mass spectrometry, or molecular based techniques, which are slow and require multi-step preparation. Our approach to an automatic, real-time solution is based on performing electrochemistry in flames<sup>1</sup>, i.e. utilisation of combustion/ionisation of bioaerosols in a premixed hydrogen/oxygen/nitrogen flame plasma, followed by gas phase potentiometric detection. When the ionised combustion plumes of particulates interact *in situ* with electrodes they can generate easily detectable potential differences. This signal should in principle be related to the size, density and composition of the original particulates, providing therefore a novel method for counting and identifying airborne organic species. By following this methodology, the detection has a physical basis, which means robustness and high sensitivity, while the signal is intrinsically amplified by the volume expansion due to combustion.

Previous work in our lab has shown that detection of latex beads can be performed in flames by means of potentiometry.<sup>2</sup> In this study we have used pollen and spore grains as model bioaerosols, the detection of which still lacks an automated solution. An overview of the state-of-the-art is first given, followed by the instrumentation details of the current concept. Its capabilities are presented by means of potentiometry results coupled with high-speed video recordings of the grains' combustion.<sup>3</sup> It is demonstrated how detection of single pollen grains can be achieved by zero current potential measurements, giving signals of the order of 500 mV and useful patterns that can potentially differentiate between species. Finally, the strengths and weaknesses of the method are discussed in the wider context of ambient air monitoring.

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## Instrumentation Based On Wet Sampling Techniques With On-Line Detection

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#### ABSTRACT

A group of air monitoring instruments uses a solution to absorb soluble gases for sequential analysis. In some cases the gas stripper is connected to an wetted particle stripper allowing also sequential analysis. Usually water soluble gases are sampled whereas the particulate matter is entirely collected. Both the gas stripping and PM stripping mechanisms serve as an powerful enrichment tool. Dynamic enrichment factors vary between  $10^4 - 10^6$ . Some applications like ion chromatography enable in liquid enrichment by concentrator columns revealing an extra enrichment factor up to  $10^2$ . Typical specification is a detection limit is 0.05 µg/m<sup>3</sup> with a time resolution of 5 to 60 minutes. Another discriminating factor is the ability for dynamic stripping. Classical methods use dry coated denuders, filters or impactor plates which generally suffer from capacity problems and artifact formation. Dynamic stripping is a way to overcome this issue.

Three groups of instruments can be distinguished. The first group being the coil based gas collectors for subsequent analysis of a special set of trace gases. Examples are the Lopap (Quma) for HONO and HNO<sub>3</sub>, the AiRRmonia (Mechatronics) for NH<sub>3</sub> and the Aero Laser for H<sub>2</sub>O<sub>2</sub> and HCHO. The second group offer a wide range of water soluble gases and PM ionic species to be measured by ion chromatography. Examples are the MARGA (Applikon), see figure and AIM (URG). Depending on the configuration simultaneous determination of trace gases like NH<sub>3</sub>, HNO<sub>3</sub>, HCl, HF, SO<sub>2</sub> and PM ions like SO<sub>4</sub>, NO<sub>3</sub>, PO<sub>4</sub>, Cl, C<sub>2</sub>O<sub>4</sub>, NH<sub>4</sub>, Na, K, Mg, Ca are possible. Last group are the samplers for PM. This group generally offer the highest enrichment factors. Examples are the PILS (Metrohm, BMI) for ions, SAES (OEI) for metals and the VACES for health related

determinations.

Due to the complex matrix and relatively low concentrations ambient air quality monitors like the wetted based, are generally poorly tested on accuracy in the applicable measuring range. Usually methods are intercompared at field campaigns. Positive exceptions are chamber verification tests like FIONA for HONO.



On research level wet sampling instrumentation is applied for the on-line measurement of many species like BC, EC, total and non soluble OC as well as the oxidative potential of PM. With respect to the gas stripping function the analogy with the respiratory pathways is appealing. Depending on the affinity with the wetted tissue reservoir health adverse gases will remain in the human body. Due to the increased humidity a significant fraction of the inhaled particulate matter will grow in size and also impact in the lungs.

## **Source Contribution - An Alternative Metrics**

*Xavier Querol* C S I C, Spain

## ABSTRACT

## Application And Limitations Of Satellite Remote Sensing Technology For Estimating Air Emissions And Concentrations Of Pollution At Ground Level In Low-Latitude Climates.

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#### ABSTRACT

Space science and technology may provide important tools in the study and assessment of national, regional and local air quality. However, the application of space-based observation of atmospheric pollutants within the lower troposphere requires further research, development and collaboration.

This paper considers the role of satellite observations in the assessment of ambient, ground-level air quality in the Niger Delta. The methodological approach to assessing concentrations of air pollutants from satellite sensors over the Niger Delta is discussed, and the particular limitations of the use of satellite sensors in this situation are identified. Whilst satellites are currently playing a significant role in the assessment of global air pollution and the trans-boundary transport of air pollutants, the technology is faced with limitations in assessing ground level concentrations of pollutants. These restrict the extent to which both pollution sources and receptors (predominantly human, but also sensitive ecosystems) can be accurately assessed.

There is need for research to improve the capability of satellite sensors to observe atmospheric pollutants within the lower troposphere, where pollution have the most direct ecosystem and human impact, taking into consideration the various climatic conditions within the lower latitudes. Further research also needs to be done in developing algorithms that can suitably extract tropospheric column of air pollutants from observed total column measurements. The sensors will need to be able to monitor specific air pollutants in order to apportion level of pollution resulting from common anthropogenic activities such as biomass burning, gas flaring, transportation and energy generation. This will support policy makers in devising appropriate legislations and policies to effectively manage air pollution.

## The German Ultrafine Aerosol Network (Guan): Routine Measurements Of Particle Size Distributions And Soot

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#### ABSTRACT

The German Ultrafine Aerosol Network (GUAN) is a cooperation of research institutes and public service institutions with the aim of improving our picture of the health and climate-relevant properties of atmospheric aerosols (Birmili *et al.*, 2009). Besides the measurement effort, the network also ensures a uniform quality assurance and quality control measures, data processing, and dissemination of the data. The body of measured PM metrics includes:

- sub-µm particle number size distributions
- non-volatile (300°C) number size distributions
- soot mass concentrations
- size-segregated chemical composition
- particle hygroscopicity

Figure 1 illustrates the location of the observation sites within Germany. Figure 2 illustrates some exemplary differences of the particle size distributions occurring at the observation sites. A main factor governing the total particle number is the proximity to urban sources such as traffic. Major factors governing soot concentrations and total particle mass are altitude, season, and air mass. It also became evident that in Central Europe, the particle concentration mass shows several episodic maxima per year that are linked to synoptic meteorology.

GUAN is embedded in the system of European observation networks that now start to include ultrafine particle information (EMEP, EUSAAR etc.). GUAN.

The presentation will highlight the experimental approach including quality assurance measures, and provide an overview of the first two years of measurement data.

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Figure 1. Measurement sites in GUAN for continuous aerosol observations.





## The UK Particle Number Measurement Network

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#### ABSTRACT

In 1998 the United Kingdom government initiated an ambient air monitoring network that included Condensation Particle Counters and Scanning Mobility Particle Sizers generating data on number concentration and size distribution, on a continuous basis. Other parameters are measured within the network that will also be described briefly within the talk.

Since 1998 the hardware, systems and procedures have all changed in response to operational needs, international developments and other factors. The talk will focus on the current operation of these instruments, with emphasis on the quality assurance / quality control (QA/QC) procedures that provide calibration to the network, and mechanisms that have been developed in other monitoring networks to assist smooth operation and high data capture.

As examples, the talk will describe:

- changes to the sampling system to control humidity and reduce internal contamination
- calibration and QA/QC carried out on site and at the laboratory
- on-line data and diagnostics collection that allow rapid fault detection and higher confidence in final data.

Some of the results from these long data sets will also be presented.

## Personal Monitoring Of Exposure To Black Carbon

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#### ABSTRACT

Black Carbon (BC) is a fraction of PM that is typically linked to traffic sources and diesel vehicles in particular. There is a growing consensus that traffic related air pollution is more toxic than the general air pollution mixture and a number of studies have observed an association between health effects and the proximity of the residence to major roads.

We have monitored personal exposure to BC using  $\mu$ -aethalometers. 16 people (8 couples) were selected for a pilot study in Flanders (Belgium). Each partner was given a  $\mu$ -aethalometer and in addition ambient air at their home address (street side) was monitored for comparison. Each couple/location was measured sequentially for one week over an 8 week period (2<sup>nd</sup> May 2010 – 8<sup>th</sup> July 2010). Whereabouts were simultaneously registered with a GPS equipped PDA and activities and trips were annotated by the participants in an electronic diary (PARROTS).

Initial results indicate that there are important differences between the partners living at the same address. Differences can be attributed to concentrations encountered at different locations and during different activities. Average outdoor concentration at the home addresses is 1323 ng/m<sup>3</sup>, average concentration while in transport is 6445 ng/m<sup>3</sup>. Exposure is lowest when sleeping (1153 ng/m<sup>3</sup>).

Participation to traffic seems especially important. Although the participants to the pilot only spend 6% of their time in traffic, this time represents ~25% of their exposure. Exposure in traffic is highest while travelling by car or by bus. There are few indications of indoor sources.

We have demonstrated that exposure analysis can be significantly improved by determining more accurately where people spend their time. People are exposed to concentrations occurring in the areas where they are active at that time, which during the day is very often not at their home address. Location, time of day and the microenvironment are essential parameters to determine exposure to pollutants with a high spatial variability such as BC, NO<sub>2</sub> or Ultrafine Particles.

## Development Of A New Measuring Bike For Mapping Dust Levels In Urban Environments: The Aeroflex Bike

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 <sup>2</sup>IMOB – Transportation Research Institute, University of Hasselt, Hasselt, Belgium

#### ABSTRACT

Fixed air quality monitoring stations have several limitations when used to assess peoples real life exposure to (ultra)fine particles and other traffic-related air pollutants. Since fixed measuring station often are expensive, only a limited number can be installed in one city. However, due to the large spatial variation of some pollutants in urban environments, the validity of the results of each of these stations is limited to their immediate surroundings. A second disadvantage of the standard (reference) equipment for fine dust is their time resolution. Therefore, we developed a measuring bike to map the different pollution levels in a city. This measuring tool will not replace fixed monitoring stations but will give some additional information in relation to peoples exposure.

Our measuring bike – called Aeroflex – is equipped with a modified P-trak for UFP concentrations and a Grimm Dust monitor for  $PM_{10}$  and  $PM_{2.5}$  concentrations. These instruments are linked to a smart-phone (or netbook) with GPS and GPRS which sends the measurements in real time to a post-GIS database at our central office. A sound level monitor, a micro Aethalometer (Magee) for BC and a vibration sensor can be added to the measuring bike but are not yet integrated in the automatic data transmission. The other pollutants can be monitored in real time. A labview application was written to monitor the current location of the bike on a Google map and map the different pollutants of previous monitoring campaigns on a color coded map.

Both the bicycle and the color coded maps can easily be used by local administrations who have little or no experience with air pollution. The results can be used to design or support local policies like mobility and road infrastructure in relation to pollution issues e.g. the optimal location of a bicycle lane next to a major road. Results of a case study showing spatial variation of UFP and BC will be presented.

## Future Urban AQ Monitoring in Europe

*Emile De Saeger* European Commission DG Env, Belgium

## ABSTRACT

## How Can Background Measurements Be Linked With Urban Air Quality

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#### ABSTRACT

Coordinated measurements of atmospheric composition and deposition fluxes were initiated in the early 1970ies through OECD project on Long Range Transport of Air pollutants. This formed the basis for a Convention on Long Range Transmission of Air Pollutants (CLRTAP) and its European Monitoring and Evaluation Programme (EMEP). This presentation will outline the developments in EMEP monitoring strategies and the requirements for EMEP monitoring in relation to site locations, methodology and QAQC-matters. An increased awareness on the strong linkages between different geographical scales (globa-regional-local) calls for a strong coordination of monitoring efforts undertaken in support to international conventions. Such coordination will improve the basis for measures and ensure a cost efficient approach. A special focus will be given to the involvement of the research community in relation to development of high precision measurements at background sites (the so-called joint EMEP-WMO/GAW supersites).

# **POSTER ABSTRACTS**

## Monitoring Of Toxic VOC In Complex Industrial Areas

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### **POSTER ABSTRACT**

The measurement of toxic VOC in ambient air is especially important in industrial areas in fast developing countries.

Complexes grow at such a speed, that control by conventional methods is not sufficient to avoid danger for the public. Although the major multinational industries are building well designed plants the surrounding smaller industries do not. Accidents, spills, badly managed waste all lead to often quite high concentrations of toxic and carcinogenic VOC in ambient air.

Synspec has long been involved in monitoring these environments with online GC. A new development is the monitoring online in the field with a combined PID / ECD system.

With such a system a whole range of toxic and carcinogenic aromatic and chlorinated compounds can be measured with a better identification.

Results from Europe and Asia will show that the system is sensitive enough to reach the required LDLs.

## Long Term Monitoring Of Reactive Gases And Water Soluble Aerosol Components At A Remote Site In South East Scotland

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#### POSTER ABSTRACT

Long term deposition of inorganic reactive gases, such as NH<sub>3</sub>, HNO<sub>3</sub>, HCI, SO<sub>2</sub> and their aerosol counter parts (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) have been demonstrated to contribute to the eutrophication and acidification of sensitive ecosystems. In addition, inorganic aerosols represent a significant proportion of tropospheric aerosols that have an important impact on human health and the climate system. Currently, PM<sub>2.5</sub> and PM<sub>10</sub> aerosols are mainly monitored by bulk mass methods. This however gives very little information on the contribution of different aerosol compounds to the total mass and on aerosol sources. Long term real time measurements of chemically speciated inorganic aerosols and their precursor gases are needed to understand the sources of emissions, and aerosol processes in the atmosphere in order to implement effective emission reduction measures.

The MARGA (Monitoring instrument for AeRosols and reactive Gases, Applikon Analytical BV, Netherlands) is an instrument that provides long term real time (hourly) measurements of water soluble inorganic aerosols (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>) and their gas precursor (NH<sub>3</sub>, HNO<sub>3</sub>, HNO<sub>2</sub>, SO<sub>2</sub>, HCl). The MARGA is based on a wet chemistry method that utilises rotating annular wet denuders for the capture of reactive trace gases and steam jet aerosol collectors (SJACs) for the collection of water soluble aerosols. Analysis is performed by online ion chromatography, providing hourly concentration values. Since June 2006 a MARGA has been operated continuously at Auchencorth Moss in South East Scotland. The site is a European 'Supersite' within the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP).

Annual average concentrations ranged from 1.77  $\mu$ g m<sup>-3</sup> to 1.06  $\mu$ g m<sup>-3</sup>, 0.10  $\mu$ g m<sup>-3</sup> to 0.12  $\mu$ g m<sup>-3</sup>, 0.27  $\mu$ g m<sup>-3</sup> to 0.71  $\mu$ g m<sup>-3</sup> for NH<sub>3</sub>, HNO<sub>3</sub> and SO<sub>2</sub> respectively, from June 2006 to December 2009 at the site. High concentrations of NH<sub>3</sub> and SO<sub>2</sub> were frequently linked to wind direction, with the peaks in NH<sub>3</sub> concentrations associated to local poultry farms, where as peaks in SO<sub>2</sub> concentrations could be linked to coal fuelled power stations. Long range transport, on the other hand, could be used frequently to explain high concentration events of aerosols. High concentrations of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, could be related to air masses originating over the UK, Western Europe or Eastern Europe and Russia, whereas high Na<sup>+</sup> and Cl<sup>-</sup> concentrations could be linked to air masses originating either over the Atlantic Ocean or the Arctic.

The result of long term monitoring using the MARGA system has led to a greater understanding of atmospheric composition and the ability to attribute sources following large pollution events at Auchencorth Moss.

## Establishing a Network of Electrochemical Sensors to Enhance Understanding of Urban Air Pollution

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d: Centre for Mathematical Sciences, University of Cambridge

#### POSTER ABSTRACT

Urban air quality issues are becoming an increasing environmental concern in the UK and further afield. As a result, it has become more important to study the behaviour of pollutants in urban environments and to better understand their sources. The development of a mobile sensing system at the University of Cambridge has been furthered to incorporate the same electrochemical sensors for CO, NO and NO<sub>2</sub> into a dense urban network capable of capturing data with high temporal resolution for several months. Laboratory tests have established that the sensors used respond well to parts-per-billion levels of the relevant target gases. Preliminary results from a three month campaign show large variation in concentrations measured, with wind speeds and directions important. Bivariate polar plots, relating concentrations to wind behaviour, are one type of tool being used to analyse the data.

## Chemical Characterization of PM<sub>10</sub> at Melpitz site in Germany – Test of an Online Wet Chemical System for Simultaneous Quantification of Gases and Water Soluble Ions (MARGA)

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#### POSTER ABSTRACT

The new sampling system MARGA (Monitor for Aerosols & Gases in ambient Air, Applikon Analytical, NL)[1] for a semi-continuous and simultaneous quantification of water soluble ions in particulate matter and their related gas phase components is tested. The MARGA is able to measure the gases HCl, HNO<sub>2</sub>, SO<sub>2</sub>, HNO<sub>3</sub> and NH<sub>3</sub> as well as the inorganic components Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> in the particle phase with a time-resolution of one hour. After passing a Teflon coated PM<sub>10</sub> inlet the sample air enters a Wet Rotating Denuder (WRD) where the water-soluble gases diffuse into an absorbance liquid. Connected to the WRD is a Steam-Jet Aerosol Collector (SJAC) which is used to collect the particles) [2]. Due to a super saturation of water vapour in the SJAC particles grow rapidly into droplets. These droplets containing the dissolved inorganic ions are collected in a cyclone. The resulting liquid solutions of the denuder and of the SJAC are analyzed online using an anion and a cation chromatograph. The MARGA transfers 1 m<sup>3</sup> air per hour into two 25 ml liquid samples and has a detection limit below 0.1 µg/m<sup>3</sup>. The ion chromatography system is calibrated by the use of an internal standard (LiBr). The MARGA was remotely accessible and a visit is necessary only once a week. The MARGA operates at the research station of the Leibniz Institute for Tropospheric Research in Melpitz, Germany (12°56'E, 51°32'N, 86 m a.s.l.) [3]. The station is located 50 km north-east of the city of Leipzig near the river Elbe in a flat terrain without noteworthy anthropogenic emissions in the nearby surroundings. At the research station Melpitz it is possible to compare the MARGA with other instruments, e.g. with the gas analyzer for SO<sub>2</sub> (UV-fluorescence) or with the water soluble ions in daily samples of PM<sub>10</sub> (DIGITEL-high-volume-samplers).

The new system has some advantages for the chemical aerosol characterization:

- a) Time resolution of one hour for concentrations of water-soluble ions in particles and their related corresponding trace gases.
- b) Artifact-free quantification of volatile species.
- c) Online analysis with remote control.

A data yield of over 90% was achieved since the launch of the MARGA in October 2009. Results of continuous measurements and same comparisons are shown. The results of MARGA are in very good agreement with this of common measuring instruments, e.g. with the SO<sub>2</sub>-monitor and with the water soluble ions in daily  $PM_{10}$  filter samples. The comparison between the MARGA and filter measurements for nitrate indicates a negative artifact in the filter measurements in July 2010 (high mean temperature of 22°C). Due to the volatile behaviour of  $NH_4NO_3$  evaporates from the particle phase as  $HNO_3$  and  $NH_3$  and thus ions cannot be quantified correctly with filter measurements.

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## Real-Time Diagnostics Of A Jet Engine Exhaust Using An Intra-Pulse Quantum Cascade Laser Spectrometer

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#### **POSTER ABSTRACT**

It has been demonstrated that an intra-pulse scanned 4.86 micron quantum cascade laser spectrometer may be used to obtain real-time diagnostics of the amounts of carbon monoxide, carbon dioxide, and water, in the exhaust of an aero- gas turbine (turbojet) engine operated in a sea level test cell. Measurements have been made of the rapid changes in composition following ignition, the composition under steady state operating conditions, and the composition changes across the exhaust plume. The minimum detection limit for CO in a double pass through a typical gas turbine plume of 50 cm in diameter, with 0.4 seconds integration time, is approximately 2 ppm.

## Gas Real-Time Sensor Analysers For Air Quality Monitoring Based In Nanotechnology

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#### POSTER ABSTRACT

The development of micromachined gas sensor devices with optimized selectivity and sensitivity, has received much interest in recent years. They provide the ability to detect the presence of a non healthy gas concentration with high energy saving and low cost taking in advance the rapid progress in micro and nanofabrication processes. However, fundamental materials and processing issues, which are critical for a high-performance gas sensor, need to be assessed [1-3].

O<sub>3</sub>, CO, NO<sub>2</sub> and H<sub>2</sub>S complete analysers have been developed for air guality monitoring, based on semiconductor oxide sensor nanotechnology. A metal oxide sensing layer, prepared using nanopowders, is deposited on top of an integrated microheater structure. The substrate consists on a dielectric membrane, comprising a polysilicon heating resistor and a pair of interdigited platinum electrodes. More details on typical sensing substrates can be found elsewhere [4,5]. Once, gas molecules are absorbed on the active surface, the resistance of the layer changes. Changes in resistance response over the time are related with changes of gas concentrations. The sensor that we have implemented have been adjusted and calibrated in laboratory under controlled atmosphere conditions. Additionally, sensors implementation has required the development of a specific datalogger. This new equipment (sensor + datalogger) provide a full solution on portable gas-monitor equipments, including wireless communications such as GSM/GPRS, ZigBee or Bluetooth. To internal data storage a SD card is provided. Full gas-monitor is power supply in with 12 Vdc. In this way, optional solar panel power supply is also available improving energy efficiency and providing a free mobility solution to the monitor. It makes possible to install it practically everywhere. The data registered by the monitor can be (remote) download and pre-process using specifically developed PCsoftware. This analysers have been tested on several real applications including:

- Ozone and nitrogen dioxide monitoring on top of an air quality reference cabin.

- Carbon monoxide monitoring in side of a traffic tunnel, or for early fire detection in forest.

- Hydrogen sulphide monitoring in a waste water industrial plant.

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## Trace Gas Detection Using Quantum Cascade Lasers. From Laboratory Analysis to Atmospheric Measurements.

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#### **POSTER ABSTRACT**

Quantum Cascade Lasers (QCL's) have proven themselves to be effective tool for mid-IR spectroscopy [1] in both the lab and for in the field measurements. We present lab based measurements of greenhouse gasses when buffered with Nitrogen, Carbon Dioxide and Helium. We also present a 4 channel pulsed QCL absorption spectrometer (4C-PQCLAS) that gives 'on the fly' concentrations of 4 atmospheric greenhouse gases. When the data recorded is post analysed other gases present in the sample may also be detected. The 4C-PQCLAS has proved itself a useful tool for both ground level and aircraft based measurements [2],[3].

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## Source Apportionment Of PM Concentrations Using NOX As A Tracer For Primary Particles

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#### **POSTER ABSTRACT**

Assessing the effectiveness of measures to manage PM<sub>10</sub> and PM<sub>2.5</sub> requires quantification of the contributions of PM from different sources. However, analysis of PM chemical composition is rarely available.

As an alternative co-located NO<sub>X</sub> measurements have been successfully used as a tracer for primary PM in London<sup>(1)</sup> and Paris, to apportion PM concentrations between primary and non-primary sources. Despite the emphasis on PM abatement from the Euro emissions standards, tailpipe emissions of  $PM_{10}$  have increased relative to those of NO<sub>X</sub> in both cities The apportionment approach also suggests that improvements in  $PM_{10}$  concentrations in London and Paris between 2000 and 2009 can be mainly explained by decreased concentrations of  $PM_{10}$  from regional sources rather than tailpipe emissions from each city. It is also apparent that the regional PM around the Paris conurbation has shown a greater decrease than that affecting London.

In the absence of measurements of PM composition for both cities, Lagrangian Particle Dispersion Backward simulations (LPDBS) analysis was undertaken to seek source regions for the long-range transported PM<sub>10</sub>. FLEXPART LPDBS were analysed using the method proposed by Hirdman et al<sup>(2)</sup>. This analysis suggested that PM<sub>10</sub> in the London region maybe linked to a wider range of distant maritime source areas than PM<sub>10</sub> in the Paris region. This implies a greater contribution from sea salt which may render London less sensitive to changes in European emissions of PM precursors when compared with Paris.

There is a need for more measurements of PM composition and new methods to integrate composition and information provided by LPDS for determine the relative contribution of regional and local source regions to the annual mean  $PM_{10}$  concentrations to address the policy question directly.

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