Air Analysis - out of the laboratory and into the field

NPL National Physical Laboratory

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Air Analysis

out of the laboratory and into the field

Conference and Exhibition

Arranged by the
Automation and Analytical Management Group
Royal Society of Chemistry,
Gas Analysis and Sensing Group
and The National Physical Laboratory

Thursday 15th May 2008

National Physical Laboratory
Teddington, Middlesex, TW11 0LW, UK

Email: conference@aamg-rsc.org
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Air Analysis -
Out of the Laboratory and into the Field

Conference with Exhibition

Thursday 15th May 2008
The National Physical Laboratory, Teddington

10:30 **Registration and Coffee**

Morning Session: Chairman: Peter Woods, National Physical Laboratory, Teddington

11:00 ***Real-Time Measurements Of Reactive Gases And Water Soluble Aerosol Components***
Marsailidh Twigg
Centre for Ecology and Hydrology, Edinburgh

11:30 ***Real-Time Mobile Monitoring Of Vehicle Emissions***
Karl Ropkins
University of Leeds, Leeds

12:00 ***Requirements And Practical Aspects Of Quality Assurance For Real Time Field Data***
Paul Quincey
National Physical Laboratory, Teddington

12:30 Lunch & Exhibition

Afternoon Session: Chair: GASG

14:00 ***Development And Opportunites For Micromachined Miniature Mass Spectrometer Systems***
Alan Finlay
Microsaic Systems, Woking

14:30 ***Portable FTIR Systems***
Dominic Duggan
Quantitech, Milton Keynes

15:00 ***Using Diffuse Optical Reflections In Gas Detectors Based On Tunable Diode Laser Spectroscopy***
Dackson Masiyano
Cranfield University, Cranfield

15:30 Tea / Coffee

Optional Visit To NPL Laboratories

ABSTRACTS

REAL-TIME MEASUREMENTS OF REACTIVE GASES AND WATER SOLUBLE AEROSOL COMPONENTS UNDER FIELD CONDITIONS

Marsailidh Twigg,[1,2] Chiara Di Marco,[1] Rick Thomas,[1,3] Gavin Phillips,[1] Massimo Vieno,[1,2] Neil Cape,[1] David Fowler[1] and Eiko Nemitz[1]

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ABSTRACT

Inorganic reactive gases such as ammonia (NH_3), nitric acid (HNO_3), sulphur dioxide (SO_2) and their associated aerosol chemical species (NH_4^+, NO_3^-, SO_4^{2-}) provide inputs of N and S to sensitive semi-natural ecosystems, contributing to acidification and eutrophication. In addition, the ions are a significant fraction of tropospheric aerosol with impacts on human health and the climate system. Real-time measurements of reactive gases and water soluble aerosols are invaluable in understanding the controls of concentrations, such as atmospheric transport, chemistry and meteorological variables. More extensive datasets are urgently needed to assess the performance of chemical transport models (CTMs) used to quantify the deposition of various compounds to a surface, air quality, and climate change. For example, the modelling of critical loads is used to combat the adverse effects to ecosystems such as acidification and eutrophication, as well as to provide information for policies such as the EC National Emission Ceilings Directive (2001/81/EC).

Over the last three decades there have been rapid improvements in the techniques used to provide real time measurements of gas and aerosol concentrations in the field. This has been achieved through modifications of established laboratory techniques such as ion chromatography, absorption spectroscopy and mass spectrometry. Examples of instruments in the field using these techniques include tunable diode laser absorption spectrometer (TDLAS), aerosol mass spectrometer (AMS), and a novel Monitoring instrument for AeRosols and Gases (MARGA) which uses on-line chromatography for analysis. The development of the above instruments has provided more precise and accurate measurements of concentrations due to increased sensitivity and selectivity of the instrumentation. The work presented here demonstrates the application and suitability of these instruments in quantifying reactive gases and water soluble aerosols in the field.

REAL TIME MOBILE MONITORING OF VEHICLE EMISSIONS

Karl Ropkins
Institute for Transport Studies
University of Leeds

ABSTRACT

Despite significant on-going improvements in associated emission control technologies, traffic-related pollution remains a significant air quality concern, particularly in urban areas. Historically, laboratory-based dynamometer testing has been most widely used to collect direct vehicle emission measurements. However, such conventional drive cycle testing is not considered strictly representative of vehicles under real driving conditions, and divergence between emission models (based on dynamometer data) and real world measurements (e.g., tunnel, inverse dispersion, remote sensing, probe vehicle and car chaser studies) is widely reported. This presentation provides an introduction of such vehicle emissions monitoring methods, mainly focusing on the collection of real time mobile measurements that can be used to characterise ‘microscale’ emission effects. Monitoring requirements (sampling resolution, instrument load, robustness, etc.) and validation procedures are discussed. Example systems and data sets are used to demonstrate the range of information that can be obtained. Finally, the scope for the introduction of novel instrumentation is also considered.

REQUIREMENTS AND PRACTICAL ASPECTS OF QUALITY ASSURANCE FOR REAL TIME FIELD DATA

Paul Quincey, Rod Robinson, Nick Martin
National Physical Laboratory, Teddington, Middlesex TW11 0LW

ABSTRACT

Whenever a new technology or instrument for air analysis becomes available, there are many steps that need to be taken before data can be compared reliably with those from other techniques. When data is to be used for regulatory reporting purposes, for example air quality measurements to show compliance with EU Directives, detailed procedures are set down both for testing instrument characteristics such as linearity and cross-interference, and for ongoing checks and calibrations during operation. These procedures and mechanisms need to be addressed by anyone aiming to enter the market for regulatory measurements.

The talk will outline four main areas:

- the metrology framework that is in place to help provide credibility to measurements (eg traceable calibration, uncertainty, international comparisons)

- requirements of legislation (eg EU Directives, CEN standards, “equivalence”)

- practical examples of laboratory validation (eg test chambers, MCERTS certification)

- practical examples of quality assurance for real-time instruments used in the field for regulatory purposes (eg air quality networks, continuous emission monitoring).

DEVELOPMENTS AND OPPORTUNITIES FOR MICROMACHINED MINIATURE MASS SPECTROMETER SYSTEMS

Alan Finlay
Microsaic Systems
Woking, Surrey

ABSTRACT

Mass spectrometers offer unrivalled specificity and sensitivity over alternative detectors such as ion mobility and infra red spectroscopy, and are regarded as the gold standard in analytical chemistry. Indeed, GC-MS systems are often used to calibrate other kinds of detectors during their manufacture and test. However, most GC-MS systems have the major drawback of being heavy and power hungry, and therefore have limited deployability. For these reasons, several groups have been attempting to develop miniature mass spectrometer systems for various field applications ranging from detection of explosives and chemical weapons to environmental monitoring. Microsaic Systems has been developing chip-scale mass spectrometer technology for several years, and the author will give an overview of Microsaic's technology, plus some of the markets and applications for such devices.

PORTABLE FTIR SYSTEMS

Dominic Duggan
Quantitech Ltd

ABSTRACT

The gas analysis in industrial sites, work-place safety related measurements and accident situation has some specific requirements. High specificity, high sensitivity, portability and ease to use.

The traditional approaches include the use of an array of simple electrochemical detectors, sophisticated analytical instruments such as GC with different detectors and a mass spectrometer and manual sampling and lab analysis

Each has particular disadvantages. Electrochemical detectors are suitable for only a small range of compounds and the response to unknowns may be unpredictable. GC and GC/MS systems are large, complex and may be slow to respond. While they can be highly sensitive and precise, the operator may need specialist training to operate the system and interpret data.
Manual sampling and lab analysis requires a specific sampling method for each type analyte and can take several days to produce a result.

The Gasmet DX4030 is unique solution combining the specificity of sophisticated analytical methods with robust and easy-to-operate on-site measurements
Based on FTIR technology to give high specificity, rapid, multicomponent analysis. The analysers have an extremely robust design – with 10 years experience from portable FTIR systems used on industrial sites.

Analysis done on the DSP processor in the analyzer, measurement data is transferred with wireless Bluetooth connection to a rugged PDA. The system requires no analytical experience at all to operate but all spectral data is available for further processing if needed.

Gasmet Dx-4030 is battery operated to give about 2.5 hours of continuous use. The sample is drawn through a wand probe by a pump in backpack and into the unheated sample cell. All the key components (interferometer, sample cell, electronics) are just the same as any other Gasmet, with minor modifications.

The analyser uses twin Digital signal processing boards with results displayed on a rugged PDA via a Bluetooth connection between the analyzer and PDA.

A single zero calibration with Nitrogen or clean air is al that is required before measurements are made.

The standard configuration includes the analyzer, back-pack, battery + charger, power source, filter, TDA Recon PDA + Calcmet Lite – software and basic application (APP-154). This is already a working instrument – unlike some competitors'

offerings. Optional equipment: Extra battery, transport case, Calcmet Pro – software extension

The Calcmet Lite Software runs on PDA (Windows Mobile) and is very easy to use, no previous experience with analytical instruments required. In concept similar to Calcmet, with .INI file for parameters .SPE files for spectra

Analyser hardware status can be checked, the parameters are stored with every analysis. Zero calibration procedure is simplified with a warning if zero is faulty. The loading of application to the DSP Calcmet running on a PC. PDA is really used just for displaying and storing the results

Sample flow rate ensures latest data displayed so that the user has a full analysis available every 5 seconds. The fields change colour to indicate alarm status and a warning is displayed if unknown compound detected

The Calcmet Lite running on the PDA saves the sample spectra and displays the results, spectra are stored in spe. and bkg. formats and can be easily transferred to a PC, results are saved in .txt format. All of the basic saving options from Calcmet are carried over to the new system. Calcmet Pro is required for situations where unknown gases are expected (the Dx-4030 can be used for just taking samples, analysis can be done later on)

Standard application LIB-001: H2O, CO2, CO, SO2, CH4, N2O + selection of 10 compounds of interest are pre-programmed on DSP. H2O and CO2 are calibrated specifically. Other compounds are non-instrument specific references

Gasmet DX-4030 applications include:

First responders:

- Fire brigades, Emergency Response teams etc. (HAZMAT)
- Application: Identifying and quantifying of Toxic Chemicals after accidents
- If unknown is present, stored sample spectra can be transferred to laptop for further analysis with Calcmet Pro (Library Search & Spectrum Match)

Industrial hygienists / Indoor air-quality measurements:

Detection of potentially harmful / toxic compounds in the workplace air

- Perchloroethylene in commercial dry cleaning
- Cargo container fumigation (PH3 etc.)
- Car painting / other factories with large scale painting operations (Volatile Organic Compounds)

Consultants / Plant operators:

Leak detection in different processes

Scientific Researchers:

Applications vary: leachate studies, possibly biogas measurements

Soil gas measurement – Chlorinated VOC’s in contaminated soil

Process vent exhaust

Hospital applications

- various anaesthetic gases in operation rooms or in gas storage areas
- Ethylene oxide for sterilization

- Methyl methacrylate in artificial joint replacement operations

The Gasmet DX-4030 Advantage

Multicomponent capability (up to 25 with PDA)
Selective; much lower cross-interferences than with NDIR or with other spectrometers. Interfering components automatically accounted for in the software
Possibility to identify unknown components
Real-time measurement
Fast response time
No Span calibrations
Easier to use than previous Gasmet's with the new PDA interface & factory-made analysis settings
Easy to upgrade application
Just user training; no need for an expert operator
Reasonable price for truly portable gas analyzer
More specific and reliable than detectors, faster and more flexible than GC

USING DIFFUSE OPTICAL REFLECTIONS IN GAS DETECTORS BASED ON TUNABLE DIODE LASER SPECTROSCOPY

D. Masiyano, J. Hodgkinson and R.P. Tatam
Engineering Photonics Group, School of Engineering
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ABSTRACT

The advantages of using tunable diode laser absorption spectroscopy (TDLAS) for trace gas sensing include; fast response times, high sensitivity and high target gas selectivity. However, the sensitivity of many practical TDLAS systems is limited by the formation of unintentional Fabry-Perot interference fringes in the optical path between the source and detector. Thermal and mechanical instabilities mean that fringes can not be removed by simple subtraction. Techniques for eliminating or reducing the amplitude of the fringe signal include: (a) careful alignment using wedged windows, (b) mechanically oscillating the path length with external devices, (c) use of alternative modulation waveforms and (d) postdetection filtering [1]. In general, these measures are effective in limited circumstances, add to instrument complexity and can be difficult to maintain in field instruments.

In recent years, there has been interest in using diffuse reflections within the optical path in the following diverse areas; use of remote laser pointer style gas detectors where the light is backscattered from a rough surface at ground level and use of integrating spheres as multi-path gas cells.

We have taken this concept further by investigating the deliberate use of diffuse reflections in TDLAS as a means of eliminating interference fringes. This approach has several potential benefits: (a) reduced complexity and costs in instrument manufacture, and (b) making systems less susceptible to misalignment, thereby increasing field robustness. However, the use of diffuse reflections introduces laser speckle that can contribute a random, rather than periodic, uncertainty to gas measurements.

We have established a method for quantifying the uncertainty due to speckle and investigated methods of reducing it [2]. We have used wavelength modulation spectroscopy (WMS) with a CCD camera that allows us to image and characterize the speckle for different optical configurations. We have tested predictions of the model by making gas measurements using WMS on the 1650nm methane absorption line. Results will be presented.

REFERENCES

1. Schiff H I, Mackay and Bechara J. Air Monitoring by Spectroscopic Techniques. Editor Sigrist M W (New York: John Wiley and sons) pp 239-333 (1994)
2. Masiyano D, Hodgkinson J, and Tatam R P, Use of diffuse reflections in tunable diode laser absorption spectroscopy: Implications of laser speckle for gas absorption measurements, Applied Physics B: Lasers and Optics, Vol. 90, No. 2, pp. 279-288 (2008)

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