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ROYAL SOCIETY OF CHEMISTRY

**Monitoring Ambient Air 2005:
Diffusive Monitoring,
Techniques and Applications**

Conference with Exhibition

**A meeting of the Automation and Analytical Management Group
Royal Society of Chemistry**

Wednesday 14th and Thursday 15th December 2005

at the English Heritage Lecture Theatre
(formerly The Scientific Societies Lecture Theatre)

London

Email: Conference@aamg-rsc.org
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**Monitoring Ambient Air 2005:
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Wednesday 14th and Thursday 15th December, 2005
The English Heritage Lecture Theatre
London

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10.00 **Registration and Coffee**

Session 1 Directives and Standardisation

Chairman: Peter Woods, National Physical Laboratory, Teddington, UK

10:30 *Meeting the Ambient Air Directives*

Andrej Kobe

DG Environment, European Commission, Brussels, Belgium

11:15 *New Techniques and Standardisation for Monitoring Ambient Air Pollutants*

Theo Hafkenscheid

NMi, Delft, Netherlands

12:00 Lunch and Exhibition

Session 2 Diffusive Sampling

Chairman: Andrej Kobe, DG Environment, European Commission,
Brussels, Belgium

13:30 *Principles and Applications of Diffusive Monitoring*

Alan Braithwaite

Nottingham Trent University, Clifton, Nottingham, UK

14:10 *A Critical Appraisal of Monitoring Techniques*

Detlef Ullrich

Federal Environment Agency, Berlin, Germany

14:50 Tea

15:20 *Formation and Fate of Ozone Precursors*

Marianne Glasius

NERI, Roskilde, Denmark

16:00 *Monitoring Ozone Precursors*

Paul Quincey

National Physical Laboratory, Teddington, UK

Thursday, 15th December, 2005

Session 3 Sorbents and Applications

Chairman: Derrick Crump, B R E, Garston, Watford, UK

10:00 *Which Sorbents to Use and When – A Practical Guide*
Liz Woolfenden
Markes International, Llantrisant, Mid Glamorgan, UK

10:30 *Design Criteria for an Automated Sampling System*
Uwe Kuhn
Max Planck Institute for Chemistry, Mainz, Germany

11:00 Coffee

11:30 *Ammonia Monitoring in the UK*
Sim Tang
Centre for Ecology and Hydrology, Penicuik, Edinburgh, UK

12:00 *New Applications For Diffusive Samplers*
Martin Ferm
IVL Swedish Environmental Research Institute Ltd, Gothenburg, Sweden

12:30 Lunch

Session 4 Sorbents and Applications

Chairman: Don Munns, Munns Environmental Ltd., Cuffley, UK

14:00 *QA/QC Traceability, Measurement Uncertainty and Accreditation in Diffusive Sampling*
Brian Goody
National Physical Laboratory, Teddington, UK

14:30 *Interpretation of Data and Dissemination of Information*
Monica Price
University of Sunderland, Tyne & Wear, UK

15:00 Tea

15.30 *Use of Diffusive Samplers to Determine Indoor Air Quality and Ventilation*
Derrick Crump
B R E, Garston, Watford, UK

16:00 *Methodology for Assessing the Packing Integrity of Adsorbents Within Thermal Desorption Tubes and Traps*
Andy Tipler
PerkinElmer, Shelton, USA

16:30 End of Conference

ABSTRACTS

MEETING THE AMBIENT AIR DIRECTIVES

Andrej Kobe

Clean Air and Transport Unit,
DG Environment, European Commission

ABSTRACT

The presentation will first give an outline of the Clean Air for Europe (CAFE) process, initiated by the Community's 6th Environmental Action plan. The Commission adopted its main deliverable, the Thematic Strategy on Air Pollution, on 21 September 2005. The strategy is defining the intermediate air quality objectives for the Community until 2020, based on the evaluation of potential for air pollution abatement, its costs and the benefits in terms of public health and ecosystems improvement. Particulate matter and ozone are the principal target pollutants. Though current legislation is already delivering a lot of benefits and will continue to do so in the near future, it is estimated that in the year 2020 roughly 270.000 EU citizens will still prematurely die due to fine particles, if nothing further is done.

An important measure outlined in the strategy, which is already on its path through the Council and the Parliament, is the revision of the air quality directives. Informing on the revision will form the core of the presentation.

Air Quality Framework Directive, 1-3 Daughter Directives and the Exchange of Information Decision are in the proposal all merged into one directive. The presentation will try to present the rationale for the proposal and some of its provisions, in particular from the perspective of the current experience with the directives. It will for example briefly address the difficulties with meeting the PM₁₀ limit values.

The proposal retains all existing monitoring provisions as well as the limit values. The indicative PM₁₀ limit value is replaced by a proposal for a PM_{2.5} concentration cap of 25 µg/m³ and a target of 10-year 20% reduction of exposure to fine particles in the Member State, as assessed by the concentrations at urban background locations. Proposal prescribes specific PM_{2.5} monitoring provisions as well as provisions on how to account for natural contribution and/or apply for possible time extension on the attainability of the limit value for up to five years, based on specific conditions. The Commission, assisted by the Data Exchange Group, is currently preparing the new reporting provisions. Changes will include a move towards a single monitoring dataflow and specific GIS based requirements for reporting on the assessment throughout the territory. It is anticipated that the new reporting provisions will represent a qualitative leap towards the implementation of INSPIRE in the air quality field.

In line with the main topic of the conference, a part of the presentation will be devoted to the role of diffusive monitoring within the existing directives as well as the new proposal.

The strategy, directive proposal and a number of accompanying reference documents, such as the WHO advice to CAFE, impact assessment and the cost-benefit analysis can be found at <http://europa.eu.int/comm/environment/air/cafe/index.htm>.

DIFFUSIVE SAMPLING WHAT'S NEW ?

Theo Hafkenschied
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NL – Delft

ABSTRACT

Diffusive sampling appears to have reached a state of maturity. A survey of recent literature sources reveals that publications in which diffusive sampling plays a key role focus mainly on applications, which are plentiful, e.g.:

- Assessment of pollutant levels in urban environments
- Assessment of personal exposure in the workplace, indoors and outdoors
- Assessment of spatial variability of pollutant concentrations, e.g. aimed at siting of monitoring stations
- Measurement of pollutant fluxes
- Establishment of indoor-outdoor relationships of pollutant concentrations.

New developments appear to focus on the search of optimal samplers for certain key pollutants: 1,3-butadiene, benzene, ozone, nitrogen dioxide, or on the search for new – although perhaps not diffusive - samplers (SPME and SPMD devices).

However, the developments in diffusive sampling have one thing in common: they are mainly results of individual efforts. As a consequence, little is known about the comparability of data obtained by diffusive sampling. This may be particularly problematic when these data are to be used for quantitative purposes, for cross-country comparisons, and not for relative purposes within single studies.

In this presentation information will be given about the state-of-the-art of diffusive sampling as a technique for quantitative evaluation of pollutant concentration levels and of further needs for developments and initiatives.

PRINCIPLE AND PRACTICE OF DIFFUSIVE MONITORING AND THE APPLICATION TO AMBIENT AIR POLLUTION

Alan Braithwaite

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Nottingham, UK

ABSTRACT

The concept of sampling ambient and workplace air for pollutants using the principle of diffusive sampling is well established. Diffusive sampling is featured in recognised validated monitoring procedures and is applicable for acid gases and VOCs. The principles utilised are based on the established gas laws of Boyle and Charles, and gaseous diffusion parameters developed by Graham and Maxwell. The paper will present a resume of the gas and diffusion laws and examine the application of Fick's law to diffusive monitoring, practical monitoring devices and the influence of ambient factors such as humidity, temperature. The factors to consider in an overall monitoring exercise will be discussed including validation of methods and overall uncertainty in results. An outline of the instrumentation needed to measure pollutants (analytes) of interest will also be included. The application of diffusive sampling for monitoring SO₂ and Nox in ambient air will be used to illustrate the technique.

A CRITICAL APPRAISAL OF MONITORING TECHNIQUES

Detlef Ullrich

Federal Environmental Agency, Berlin

ABSTRACT

About thirty years ago diffusive samplers were introduced to assess the air quality in the course of workplace surveillance in a convenient manner. The validity of workplace measurements by diffusive sampling had been shown in two EU conferences which took place in Luxembourg in 1986 and 1991.

Widening the scope of application the main areas of additional interest were ambient and indoor air quality. A good overview of this large field of application and the quality of data received was given at the "International Conference – Measuring Air Pollutants by Diffusive Sampling" in Montpellier in 2001.

This development was accompanied with the work of WG 11 of CEN/TC264 which compiled a series of European standards (EN 13528, 1 – 3, general and ambient air quality and EN 14412, indoor air quality) to set a reliable basis for validating and using diffusive samplers.

In parallel a variety of international laboratory and field tests were performed to prove the validity of different types of diffusive samplers to measure ambient air quality. Most of these tests were carried out on the basis of EN 13528 or/and in the course of the implementation of benzene references methods due to the EC Benzene Directive.

| Analyte | Organisation | Location | Date | Field-/Laboratory-Test |
|--|--------------|--------------------|------|----------------------------|
| NH ₃ | GSF | Neuherberg, D | 1998 | Field |
| Benzene | NPL | Teddington, UK | 2001 | Laboratory |
| Benzene | VITO | Mol, B | 2001 | Laboratory/Field Condition |
| O ₃ , NO ₂ , SO ₂ | VITO | Willebroek, B | 2001 | Field |
| O ₃ , NO ₂ , SO ₂ | NPL | Teddington, UK | 2002 | Field |
| NH ₃ | NMI | Zegfeld, NL | 2002 | Field |
| NO ₂ | ERLAP | Ispra, I; Paris, F | 2003 | Field + Laboratory |

The appraisal of the validation campaigns due to the Benzene Directive comprehends the combined uncertainty for each method and different experimental conditions. Taking into account the mean value of all prevailing conditions, the combined uncertainties of diffusive and pumped sampling were considered to be equal with values of about 10%.

In addition to the reports of these large intercomparison exercises there are numerous publications and studies dealing with the validation of specific diffusive sampler types for different analytes and applications mainly on ambient and indoor air quality and personal exposure. For most of these applications diffusive samplers will be used as substitute of complicated, time consuming or expensive but well established methods. Generally, the usefulness and the validity of diffusive sampling results had been shown. On the other hand, individual drawbacks and advantages of the sampler types had been outlined, e.g. the dependence of the uptake rate on the velocity of adjacent air flows.

FORMATION AND FATE OF OZONE PRECURSORS

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ABSTRACT

Tropospheric ozone is of concern due to its noxious properties towards vegetation and humans. Levels of tropospheric ozone are dominated by photochemical formation from volatile organic compounds (VOC) and nitrogen monoxide and nitrogen dioxide (NO_x). A series of VOC has been identified in Directive 2002/3/EC as ozone precursors reflecting mostly anthropogenic hydrocarbons. The term VOC covers a wide range of organic compounds, and the reactivity of VOC and their potential to form ozone varies substantially. Generally, the lifetime of biogenic VOC is much shorter than for typical anthropogenic VOC, and this affects atmospheric transport regimes (local to hemispheric scales) and fate of these compounds. On a global scale, natural emissions are the major source to VOC but the exact magnitude is highly uncertain. Thus it is important to assess the relative contribution from VOC of biogenic and anthropogenic origin to ozone formation, especially in relation to the above mentioned Directive.

Measurements of radiocarbon content of photochemical oxidation products can provide information about the sources. Such investigations have been performed for carboxylic acids and carbonyl compounds, and the results showed surprisingly high biogenic contributions (Glasius et al., 2001; Larsen et al., 2001).

Sources to ozone precursors have also been investigated using semi-continuous GC-analysis techniques and receptor modelling. In a recent study the ozone forming potential of C₂-C₉ hydrocarbons in Milan air was attributed equally to gasoline and diesel vehicle emissions (Latella et al., 2005).

M. Glasius et al. (2001) *J. of Geophysical Research-Atmospheres*, 106 (D7), 7415-7426.

A. Latella, G. Stani, L. Cobelli, M. Duane, H. Junninen, C. Astorga, B.R. Larsen (2005). *Journal of Chromatography A*, 1071, 29-39.

B.R. Larsen, A. Tudos, J. Slanina, K. Van der Borg, D. Kotzias (2001). *Atmospheric Environment*, 35, 5695-5707.

MONITORING OZONE PRECURSORS

Paul Quincey and Peter Woods

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ABSTRACT

The presentation will cover two areas:

Firstly, a brief history of national monitoring networks for hydrocarbons in the United Kingdom will be given. Large volumes of data were obtained over the period 1993 - 2000, when up to 13 sites generated hourly data for 25 hydrocarbon species very similar to the list of ozone precursors given in the Ozone Directive. Since then there has been a smaller automatic network with 3 sites monitoring BTEX and 1,3-butadiene, and 2 sites monitoring a larger range of hydrocarbons, and a larger network of 35 non-automatic sites generating fortnightly data for benzene only using a pumped method, with some sites also monitoring 1,3-butadiene using diffusive sampling. New calibration cylinder standards have been developed at NPL for automatic sites monitoring the full range of ozone precursors.

The second part of the talk will describe work at NPL to establish what information about ozone precursors can be reliably extracted from the pumped and diffusive chromatograms obtained from the non-automatic network. The results showed that of the 29 species in the Ozone Directive, data for 13 was available from the pumped samples, and data for 10 was available from the diffusive samples, with 2 species common to both methods. The results compare well with previous automatic data, and make an interesting comparison with emission inventories for the same species.

WHICH SORBENTS TO USE AND WHEN – A PRACTICAL GUIDE

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ABSTRACT

Sorbent selection : Correct selection of sorbents is critical to the success of any tube-based vapour monitoring exercise. Whether pumped (active) or diffusive (passive) sampling techniques are being employed, the two main objectives are invariably:

1. quantitative and complete retention of target analytes during sampling and
2. complete release of target analytes during desorption & analysis

A secondary objective may also be

3. selective elimination of high concentration interferences (e.g. water) during sampling.

Few people fundamentally understand all the processes involved in sorbent-sorbate interactions, so, for most of us, sorbent selection remains a happy mixture of science and art with a few guidelines/rules and known pitfalls to assist the otherwise empirical process of sorbent selection. Key parameters to consider when choosing sorbents are: - sorbent strength, reactivity (storage and desorption issues), artifact levels, hydrophobicity, temperature range, batch-to-batch variability, physical strength (tendency to form fines), desorption efficiency, known retention volume / uptake rate and impedance. A summary of the impact of each of these issues and respective guidance will be presented.

While diffusive sampling is conventionally restricted to one sampling surface (and thus a single sorbent), up to 4 sorbents can be successfully arranged in order of increasing sorbent strength for pumped monitoring. Such samplers are very versatile with respect to analyte volatility and are extensively used, however, use of multiple sorbents brings additional considerations – particularly issues of migration during storage, mis-matching of sorbents with different maximum temperatures and water retention. These issues and associated practical guidelines will also be discussed.

Validation of sorbent selection and sampler performance: Various methodologies have been described in the literature regarding validation of sampling efficiency. Examples include use of back up tubes (pumped monitoring), distributed volume sampling (pumped monitoring) and parallel monitoring of pumped with diffusive samplers & vice versa.. However, validation of desorption efficiency during analysis is equally important. This used to be a difficult and imprecise art relying on generating comparative data between liquid injection and thermal desorption under identical analytical conditions. This is one of the areas where recent developments in TD technology have had most impact. Monitoring pressures during the various stages of system operation, SecureTD-Q (quantitative re-collection of splits during both primary and secondary desorption) and electronic mass flow control of split and column flows have all made an invaluable contribution to the issue of validation of desorption efficiency. Key examples of recent TD innovations and their application to the validation of sampling and thermal desorption efficiency will be described.

DESIGN CRITERIA FOR AN AUTOMATED CARTRIDGE SAMPLING SYSTEM FOR VOC CONCENTRATION AND FLUX MEASUREMENTS

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ABSTRACT

The design criteria of an automated constant flow sampler for sequential sampling of volatile organic compounds (VOC) on adsorbent cartridges are described. Features of the system include (a) the capability to collect up to 20 sequential samples to allow for long-term air quality assessments, (b) the ability to simultaneously collect two samples from different sources (e.g. for differential flux measurements), or to simultaneously collect two samples from one single source (e.g. for Quality Assurance backup samples), respectively, (c) to simultaneously collect on two different cartridge designs from one single source to increasing the range of analytical applications, (d) the use of inert wetted surfaces to ensure sample integrity, (e) the ability to set individual sampling times, intervals and flow rates by a microprocessor control unit with significant ease of operation, and (f) the capability to store data onto non-volatile memory during sampling for a complete audit trail of the sampling sequence. Various tests in the lab and during different field applications, including enclosure measurements, aerodynamic gradient techniques and relaxed eddy accumulation (REA) measurements, in a variety of environments (temperate and tropical climate) demonstrate the versatility of the automated VOC sampler. Low technical expenses, low power consumption, a robust weatherproof enclosure, and field portability allows sampling at remote sites and locations sensitive to disturbances or with restricted access.

AMMONIA MONITORING IN THE UK

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ABSTRACT

Ammonia (NH₃) emissions are estimated to have at least doubled over the last century across Europe, concomitant with intensification of agriculture, and increase in use of nitrogen fertilizers. The main sources of NH₃ in the atmosphere are from the decomposition and volatilisation of animal wastes. Other sources include direct volatilisation from synthetic fertilizers (particularly urea), and a wide range of non-agricultural sources such as sewage, catalytic converters, wild animals and industrial processes. It is recognised that deposition of atmospheric NH₃ contributes to acidification and eutrophication processes, which can cause damage to sensitive ecosystems.

The UNECE 1999 Gothenburg protocol and the EU National Emissions Ceiling Directive (NECD) of 2010 both set emission targets for individual countries. Abatement of NH₃ emissions is also included in EU Integrated Pollution Prevention and Control (IPPC) for the intensive pig and poultry sectors.

In the UK, the DEFRA-funded National Ammonia Monitoring Network (NAMN, www.edinburgh.ceh.ac.uk/cara/) was established in 1996 to quantify temporal and spatial changes in air concentrations and deposition in gaseous NH₃ and aerosol NH₄⁺ on a long term basis. The monitoring provides a baseline in NH_x species, which is necessary for examining responses to changes in the agricultural sector and to assess compliance with targets set by international agreements. Data from the network are also used to test the performance of an atmospheric chemistry and transport model, FRAME that was developed at the same time with a special focus on NH_x.

There are currently 94 sites in the NAMN. At 57 of these sites, an active diffusion denuder methodology using the CEH DELTA (DEnuder for Long Term Atmospheric sampling) system is used to provide the main spatial and temporal patterns of NH₃ (and also NH₄⁺ aerosol) across the UK, whilst a high sensitivity passive diffusion sampler, the ALPHA (Adapted Low-cost Passive High-Absorption) sampler is implemented at a further 49 sites to assess regional and local scale variability in air NH₃ concentrations in source regions. To provide an ongoing validation of the ALPHA sampler, its performance is continuously assessed against the DELTA system at 12 sites within the network. The ALPHA sampler has also been tested in several international intercomparisons, e.g. EC ECOMONT project, and was included in the CEN TC264/WG11 pilot study into diffusive samplers for NH₃

NEW APPLICATIONS FOR DIFFUSIVE SAMPLERS

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ABSTRACT

The decreasing sulphur dioxide levels in most parts of Europe and the increasing automobile traffic, causing elevated levels of nitrogen compounds, ozone and particulate matter have created a new multi-pollutant situation. Very few long-term measurements of atmospheric HNO₃ concentrations have earlier been performed despite the fact that HNO₃ is acidifying, eutrophying and causes corrosion and degradation on many materials. Long-term measurements in Sweden have shown a tenfold decrease of the SO₂ concentration during the last two decades, but no decreasing trend for nitric acid. The two gases now have equal concentrations on a molar basis

Atmospheric corrosion is a long-term effect, the relevant research therefore does not require monitoring on a daily basis. Moreover, power supply is often not available at sites where it is of interest to study the corrosion rate of objects belonging to our cultural heritage. Besides, such measurements must not disturb the impression of the objects.

Passive, long-term integrative techniques are ideal for sampling around objects of cultural heritage because the equipment is noiseless, don't need electricity and can be performed inconspicuously and with discretion. Other advantages are that technical personnel is not needed for exposing the samplers, the samplers don't need field calibration and the measurements are made *in situ*, i.e. reactive gases such as HNO₃ are not lost in inlet tubings. A diffusive sampler for HNO₃ has been compared to denuder technique in Gothenburg, Rome and Athens and has then been used to monitor concentrations at 11 rural and 23 urban widely spread sites over Europe.

Corrosion and degradation of objects belonging to our cultural heritage also takes place inside museums. Only about 5 – 10 % of the objects in a museum are displayed. The rest are stored in small boxes or storage rooms that often lack ventilation and the objects are inspected very seldom. The concentration of organic acids such as formic and acetic acid can be very high in closed rooms. The exhibited objects are also often stored in closed display cases. A diffusive sampler can be used to measure the emission of organic acids in a small closed compartment when the volume of the compartment is much smaller than the uptake rate of the sampler multiplied with the exposure time.

Eruptions are not the only problem with volcanoes. Mount Etna is the largest single source for SO₂ in Europe. The geographical concentration distribution of HF, HCl and SO₂ has been monitored in order to demonstrate the usefulness of diffusive sampling.

Even though we spend most of our time indoors, most directives concern the outdoor air, where also most air quality measurements are performed. Indoor air was in fact the first application for diffusive samplers. Today, diffusive samplers are available for more gases and vapours and better methods are available for evaluating the results. A new diffusive sampler for elemental mercury vapour has successfully been tested in the laboratory.

References

- Aiuppa A., Bellmo S., D'Alessandro W., Federico C., Ferm M. and Valenza M. (2004) Volcanic plume monitoring at Mount Etna by diffusive (passive) sampling. *J. Geophysical Research* **109**, D21308, doi:10.1029/2003JD004481
- Ferm M., De Santis F. and Varotsos C. (2005) Nitric acid measurements in connection with corrosion studies. *Atmospheric Environment* **39**, 6664-6672
- Ferm M., Karlsson A. and Galle B. (2002) A multi-component diffusive sampler for acidic gases. *The Diffusive Monitor* **13**, 3. (www.hsl.gov.uk/publications/diffuse-monitor.htm)
- Mi Y.-H., Norbäck D., Tao J., Mi Y.-L., Ferm M. (2005) Current asthma and respiratory symptoms among pupils in Shanghai, China: Influence of building ventilation, and nitrogen dioxide, ozone, and formaldehyde in the classrooms. *Indoor Air* (accepted for publication).

A CONTROLLED ATMOSPHERE TEST FACILITY FOR TRACEABLE MEASUREMENT OF UPTAKE RATE WITH VALIDATED UNCERTAINTIES

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ABSTRACT

The NPL Controlled Atmosphere Test Facility is designed to test and calibrate field samplers over wide ranges of ambient temperature, humidity and air speed. Multiple test gas mixtures of up to thirty adjustable component concentrations can be generated with traceability to national standards and with validated uncertainties. Uptake rates may be measured in laboratory-generated, test gas atmospheres and controlled environments that can be adjusted to resemble ambient conditions in the field. This allows realistic uptake rates to be determined, even in unusual atmospheres and ambient conditions and gives improved confidence in the quality and accuracy of air quality measurements. Pumped samplers can also be dosed by extracting test atmosphere from the facility.

The performance of the facility exceeds the requirements of EN 838, allowing the ambient conditions to be better controlled and defined to ensure uniform dosing of each of the exposed diffusive samplers. This reduces the contribution that variations in sampler dosing can make to the uncertainty in their measured uptake rate.

Accurate analysis and traceable calibration artefacts are essential in determining the amount of determinand collected by diffusive samplers, but without accurate uptake rates in applicable conditions the concentration at the sampling point cannot be derived with certainty. The NPL Controlled Atmosphere Test Facility is available to manufacturers and users of diffusive samplers to determine uptake rates, with a defined uncertainty, in selectable ambient conditions and atmospheres.

THE MANAGEMENT & COMMUNICATION OF AIR QUALITY DATA IN THE TYNE & WEAR REGION.

Monica Price

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University of Sunderland.

ABSTRACT

Many local authorities monitor ambient air quality within their regions and generate a large archive of information. However, time constraints within local government have historically meant that much of this data is only used for the preparation of the reviews and assessments of air quality required by central government. Often these reviews and assessments are carried out by individual authorities (either in-house or by consultants) and fail to address regional issues that contribute to poor air quality.

It is also a requirement of both legislation and policy that the public are informed as to the quality of air in their regions and local authorities are increasingly using the world wide web for the dissemination of information on pollutants.

This paper will describe a project developed in the North East of England whereby both the database of information and the web site used to disseminate the pollution data, collected by five local authorities, is managed by Sunderland University.

Real time information on: nitrogen oxides, airborne particles (PM₁₀), sulphur dioxide, carbon monoxide and ozone is collected across the region by the five local authorities in the Tyne and Wear region. This information is polled by the University with daily checks being made on the quality of the data collected. At this stage each local authority is informed of any problems with a monitor in their region. Full reports on the data giving a regional perspective and the relationship of poor air quality to local meteorology are produced every three months. An annual report is also produced which is in a format that each local authority can submit to central government.

The web site is automatically updated daily and quality checks on the data are made by the University. Downloadable information on air pollution are both written and uploaded on to the web site by the University.

USE OF DIFFUSIVE SAMPLERS TO DETERMINE INDOOR AIR QUALITY AND VENTILATION

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ABSTRACT

Diffusive samplers are widely used for ambient air monitoring particularly for BTEX, NO₂, O₃, NH₃ and SO₂. Their usefulness for providing cost effective measurements of long term mean concentrations is equally applicable in indoor environments. Issues of method performance and appropriate sampling strategies are important for both indoor and ambient environments. For non-occupational indoor environments there has not to date been a strong legislative driver for development of methods, as in the ambient air, to verify compliance with air quality standards. However there has been sufficient scientific interest combined with the possibility of future requirements, and this has driven the preparation of standards in CEN and ISO for the diffusive measurement of some pollutants such as VOCs and formaldehyde and the measurement of ventilation. Examples include ISO 16017-2, ISO 16000-4, ISO DIS 16000-8 and EN14412.

An increasing number of countries including the UK have published air quality guidelines expressed as maximum concentrations for a defined exposure period. These are additional to recommended guidelines for indoor and ambient air for some pollutants published by the WHO. Air quality guidelines are being incorporated into Building Regulations (England and Wales) that determine ventilation, and performance targets for several pollutants are included in the revised ADF (Ventilation) that will be effective in 2006. This interest is due to recognition that indoor air quality is important for the health and well being of occupants, being the most important microenvironment for population exposure to many air pollutants, and this air quality can impact on productivity at the workplace and learning effectiveness in schools. The inhalation of pollutants indoors is also identified as a potentially important source to receptor link within contaminated land legislation.

Diffusive samplers have been applied by BRE as part of a wide range of studies of air quality in homes, offices and schools and to measure ventilation concurrent with these measurements. These studies show the usefulness and some current limitations of diffusive samplers for the study of indoor environments.

References

Silva G, Fernandes E, Tirkkonen T, Jarnstrom H, Villberg K, Saarela K, Cox C, Aizlewood C, Crump D, Brown V, Dimitroulopoulou S and Samudio M. Active versus passive sampling of VOCs in IAQ field studies in selected energy-efficient European office and residential buildings. Proceedings of Indoor Air 2005, p 816-820, 4-9 September, Beijing, 2005, Tsinghua University Press.

Crump D, Squire R, Brown V, Yu C, Coward S and Aizlewood C. Investigation of volatile organic compounds in the indoor air of a school over a one year period following refurbishment. Proceedings of Indoor Air 2005, p 659-663, 4-9 September, Beijing, 2005, Tsinghua University Press.

Dimitroulopoulou S, D Crump, S K D Coward, V Brown, R Squire, H Mann, M White, B Pierce and D Ross. Ventilation, air tightness and indoor air quality in homes in England built after 1995, BRE report BR 477, BRE, Garston, 2005.

Crump D, Brown V, Rowley J and Squire R. Reducing ingress of organic vapours into homes situated on contaminated land. Environmental Technology, 25, 443-450, 2004.

Raw G, Coward S, Brown V and Crump D. Exposure to air pollutants in English homes. Journal of Exposure Analysis and Environmental Epidemiology, 14, S85-S94, 2004.

Mohle G, Crump D, Brown V, Hunter C, Squire R, Mann H and Raw GJ. Development and application of a protocol for the measurement of indoor air quality. Indoor and Built Environment, 12 (3) 139-150, 2003.

METHODOLOGY FOR ASSESSING THE PACKING INTEGRITY OF ADSORBENTS WITHIN THERMAL DESORPTION TUBES AND TRAPS

Andrew Tipler, PerkinElmer LAS, USA
Neil T Plant, Michael D Wright, Health and Safety Laboratory, UK

ABSTRACT

For a thermal desorption analysis to be successful, the adsorbent inside each tube and secondary trap must be properly packed. Any voids caused by settlement or contraction of the packing may induce channeling of the gas flow during pumped sampling and thermal desorption. Such effects may also disturb the geometry of the 'air gap' which is critical for predictable performance in diffusive sampling. Furthermore, the adsorbent may be damaged during improper packing, rough handling or by thermal shock giving rise to small fragments (fines) that fill the interstices between the packing particles and so serve to partially block the flow of gas during sampling and desorption. Clearly, tubes and traps that are correctly packed and maintained will give better sampling and analytical performance and should generate better data as a result.

In the case of glass tubes and traps, the condition of the packing may be assessed by visual inspection. This is not an option for diffusive monitoring because of the (opaque) metal tubes normally employed and so some other means must be found. One convenient technique to assess packing integrity would be to measure pressure drop across the tube or trap while a fixed flow rate of gas is applied. While such measurements have been previously performed manually, in this work we have adapted technology available on modern thermal desorption instrumentation to automate this procedure for both tubes and traps.

A fixed pressure of carrier gas is applied to the inlets of the tube or trap and mass flow controllers on the outlets are used to ensure that a fixed flow rate of gas passes through the packing. The pressure drops across both the tube and trap are recorded simultaneously and at the start of each analysis, but prior to desorption, using sensitive differential pressure transducers. To correlate the results for the tubes using the automated method against data from manual methods, the measured pressure drop is corrected to standard ambient temperature and pressure (SATP) using Darcy's Law and the Poiseuille-Hagen equation.

The application and performance of this new technology demonstrate that the automated measurement of packing impedance provides a useful measure of the condition of that packing for operational QC and diagnostic purposes.

POSTER ABSTRACTS

NEW APPLICATIONS FOR DIFFUSIVE SAMPLERS

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POSTER ABSTRACT

The decreasing sulphur dioxide levels in most parts of Europe and the increasing automobile traffic, causing elevated levels of nitrogen compounds, ozone and particulate matter have created a new multi-pollutant situation. Very few long-term measurements of atmospheric HNO₃ concentrations have earlier been performed despite the fact that HNO₃ is acidifying, eutrophying and causes corrosion and degradation on many materials. Long-term measurements in Sweden have shown a tenfold decrease of the SO₂ concentration during the last two decades, but no decreasing trend for nitric acid. The two gases now have equal concentrations on a molar basis

Atmospheric corrosion is a long-term effect, the relevant research therefore does not require monitoring on a daily basis. Moreover, power supply is often not available at sites where it is of interest to study the corrosion rate of objects belonging to our cultural heritage. Besides, such measurements must not disturb the impression of the objects.

Passive, long-term integrative techniques are ideal for sampling around objects of cultural heritage because the equipment is noiseless, don't need electricity and can be performed inconspicuously and with discretion. Other advantages are that technical personnel is not needed for exposing the samplers, the samplers don't need field calibration and the measurements are made *in situ*, i.e. reactive gases such as HNO₃ are not lost in inlet tubings. A diffusive sampler for HNO₃ has been compared to denuder technique in Gothenburg, Rome and Athens and has then been used to monitor concentrations at 11 rural and 23 urban widely spread sites over Europe.

Corrosion and degradation of objects belonging to our cultural heritage also takes place inside museums. Only about 5 – 10 % of the objects in a museum are displayed. The rest are stored in small boxes or storage rooms that often lack ventilation and the objects are inspected very seldom. The concentration of organic acids such as formic and acetic acid can be very high in closed rooms. The exhibited objects are also often stored in closed display cases. A diffusive sampler can be used to measure the emission of organic acids in a small closed compartment when the volume of the compartment is much smaller than the uptake rate of the sampler multiplied with the exposure time.

Eruptions are not the only problem with volcanoes. Mount Etna is the largest single source for SO₂ in Europe. The geographical concentration distribution of HF, HCl and SO₂ has been monitored in order to demonstrate the usefulness of diffusive sampling.

Even though we spend most of our time indoors, most directives concern the outdoor air, where also most air quality measurements are performed. Indoor air was in fact the first application for diffusive samplers. Today, diffusive samplers are available for more gases and vapours and better methods are available for evaluating the results. A new diffusive sampler for elemental mercury vapour has successfully been tested in the laboratory.

USE OF DIFFUSIVE MONITORING FOR THE PROTECTION OF CULTURAL HERITAGE INDOORS

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POSTER ABSTRACT

In contrast to active sampling in which air is brought into contact with a detector or collector device by means of a pump, diffusive sampling relies on diffusion to bring the pollutant into contact with the collector. Compared with the pump-dependent active sampling procedure, the main advantages of the method are cost effectiveness, and simplicity. The method is suitable for simultaneous and multipoint measurements of air pollutants. Diffusive sampling is characterised by low sampling rates necessitating long sampling times. As a consequence, diffusive sampling can only provide information on integrated average concentrations over the exposure period. This feature can be viewed as an advantage in the field of artwork and cultural heritage protection as it makes it easy to determine average concentrations for the sampling period which reflect the long-term action of corrosive gases on sensible materials. Current research involving diffusive sampling of which we refer in this communication is focused on understanding the outdoor-indoor relation of pollutant concentrations and on the role of corrosive gases in the deterioration of works of art indoors. Diffusive samplers can be used as a monitoring technique because - in this specific application - the average, instead of the real time pollutant concentration is adequate for the purpose of the monitoring. They can also be used as screening devices for those locations where no prior monitoring has taken place to characterise those areas where threshold values are expected to be exceeded. As an example of the indoor application of a passive diffusive method, results of a monitoring campaign at the Uffizi Gallery and at the "Galleria dell'Accademia" in Florence where the Michelangelo's David is displayed, are here presented. The diffusion method was used to measure the distribution of some relevant gaseous pollutants in three selected room of the Gallery and, simultaneously, outdoors. Infiltration factors were quantified by calculating indoor/outdoor ratios for the measured pollutants. The study, was done within the framework of the Project MIMIC (Microclimate Indoor Monitoring in Cultural Heritage Preservation) and it is part of a more complex activity to characterise indoor air in museums. In this study we used diffusion samplers called "Analyst" which are particularly suited for long-term measurements (typically one month or more). The sampler is a modification of the open-tube design obtained by using a filter treated with appropriate reagents to trap the pollutant. The body of the sampler is a cylindrical vial with a threaded cap at one end. The pollutant is collected on a impregnated disc placed at the bottom of the vial and held in position by a stainless steel ring. To avoid turbulent diffusion inside the vessel, the open end is protected using a fine stainless steel screen. Time-weighted average concentrations of 6 relevant air pollutants were determined. Distinct trends and seasonal variation in the concentration of monthly averages for NO₂, NO_x, O₃, SO₂, HNO₃ and HONO were observed in successive monthly sampling periods which started in March 2001. For each pollutant, the indoor level was a function of its outdoor level, the air exchange rate, and the rate at which it is produced or removed by indoor chemistry and by indoor surfaces. SO₂, O₃ and HNO₃ were, as expected from their reactivity, invariably lower indoors whereas indoor NO_x and NO₂ in the majority of the sampling periods were similar to the corresponding outdoor values. It was also found that high concentrations of nitrous acid are generated via indoor chemistry through thermal reaction of NO₂ with water on surfaces. Possible implications for the conservation of artworks indoors will be considered.

DEVELOPMENT OF DIFFUSIVE SAMPLER FOR HYDROGEN SULPHIDE

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POSTER ABSTRACT

Hydrogen sulphide is not routinely measured in urban air, even if recent findings have shown that its importance is growing due to emission from catalytic converters. A simple, inexpensive diffusive sampler was developed for monitoring H₂S. In principle, diffusive sampling represents a perfect tool to characterise those areas where the limit values are expected to be exceeded and/or where alternative assessment methods are needed. Compared with active sampling, main advantages of the method are cost effectiveness, simplicity and suitability for mapping large areas. The sampler is a modification of the open-tube design (Analyst®) obtained by using a filter paper impregnated with a solution based on the use of AgNO₃ as a component of a suitable mixture. In presence of H₂S a stain of silver sulphide darkens the absorbing pad. The amount of H₂S is determined by reflectance measurements using a home-built, low cost portable reflectometer: the decrease of reflectance is proportional to the concentration of H₂S. The use of a simple reflectance reading method cuts off the time consuming, expensive laboratory analysis necessary for diffusive samplers developed to collect other pollutants. The diffusive sampler was tested in chamber and field trials. Laboratory and field tests concerning sorption efficiency, capacity and effect of humidity were carried out. The effect of wind turbulence, the interference of NO₂ and the self-consistency of the method were also studied. A typical application of the developed diffusive sampler entails a sampling time of at least one month at concentrations usual for a polluted atmosphere (about 500-1000 ppt). The results obtained are reported and discussed.

STABILITY OF LOW CONCENTRATIONS OF COMPLEX GAS MIXTURES

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POSTER ABSTRACT

Increasingly, the term “complex mixture” can be attributed to a gas mixture of only one compound at a very low concentration (ppbv levels) in a particular balance gas. In cases such as this, the challenge is to guarantee good stability of the product combined with an acceptable shelf life. To succeed in achieving this aspiration, all the steps in the gas mixture manufacturing process are clearly important and may even be critical.

The recognition of the quality of Experis[®] treated cylinders by National Metrology Institutes is evidence that as a company, Air Products can provide a very high standard of gas package in terms of the cylinder, the valve and also modified internal surface treatment.

Our expertise in the actual gas filling process combined with the discipline of rigorously applied internal operating procedures which include an analytical capability which emphasises the value of the inter-comparison of data among a number of gas mixture standards provides us with the potential to obtain and characterise very stable mixtures within a production environment.

The aim of this presentation is to show the expertise of Air Products gas mixture manufacturing capability and also provide an illustration of the long term stability of a number of mixtures which contain what are often considered to be “difficult” components. A guarantee of mixture stability of over 2 years, in concentrations which range from ppm down to less than 10ppb is in accordance with the increasing requirements of customers, particularly in the field of emissions monitoring.

PASSIVE MEASUREMENTS TO EXPLORE AND IDENTIFY THE ORGANIC AMBIENT AIR POLLUTION IN A BELGIAN URBAN AREA (MECHELEN)

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POSTER ABSTRACT

In the southern part of Mechelen, a central city in Flanders, numerous complaints had been recorded with regard to air pollution and odor nuisance. In this area, an industrial zone is present, as well as busy local traffic, a lot of housing and a passing highway (E19). In a first project, a measurement campaign was organized to identify and map the sources that contribute to the nuisance. A grid was used which contained 59 sampling locations. Six volatile organic compounds were quantified using diffusive samplers. It was concluded here that traffic was the main source that led to the complaints and that the traffic load should be reduced in a first policy measure.

It is possible however that a more complex mix of volatile organic compounds contributes to the nuisance suffered, and reported by the inhabitants. Therefore, VITO has conducted a new study where the VOC's present in the samples were identified at a selection of sampling locations. The locations represented traffic intersections, urban background and rural background. Diffusive samplers with high uptake rate were sampled for seven days which resulted in sampling volumes between 600 and 800 liters. After desorption with carbon disulfide, the samples were analyzed by GC-MS in scan - mode. Converted to ambient concentrations, detection limits were typically between 0.1 $\mu\text{g}/\text{m}^3$ and 1 $\mu\text{g}/\text{m}^3$.

The identified pollutants allowed data interpretation that had never been possible in Flanders before. Because the composition of transport exhaust is known, it was possible to identify additional pollutants emitted by industry, such as dimethylhexane or acetone. A new pollution indicator, the total organic air pollution (TOL) was defined, and its relation with benzene and BTEX-concentrations was calculated. The TOL-value gave a much better explanation for the complaints registered than only the benzene concentrations. In this study, the relationships between the benzene concentrations (representative for gasoline engines) and diesel fractions (C10-C20 alkanes, alkenes and aromatics above C13) were calculated. The diesel fraction (expressed as benzene equivalents) can rise up to ten times the benzene concentrations. In contrast with benzene, the diesel fraction is substantially higher at the highway compared to urban backgrounds. It appears to be a better indicator for traffic pollution than benzene concentrations.

RESULTS OF INDOOR AND OUTDOOR MEASUREMENTS IN THE AREA OF THE EAST OF SPAIN

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POSTER ABSTRACT

To implement the WHO's guidelines, which identify the need to evaluate human exposure to air pollutants in indoor and outdoor air, so as in accordance with the Plan of Action of the European Commission and with the Fourth Ministerial Conference on Environmental and Health, which was held in June 2004 in Budapest, a network "Childhood and Environment Surveillance Scheme INMA" was set up in different geographical regions of Spain in an attempt to establish the influence of air pollution in indoor and outdoor air, before and after birth on child health.

For this study, outdoor, indoor and personal exposure to air pollutants are considered and the air pollutants have included, volatile organic compounds (VOC's) and NO₂ in the Valencia area, big city located in the east of Spain, in fourth sampling campaigns of two and seven days, distributed over 2004 and 2005 .

VOC's and NO₂ were collected from the ambient air by diffusive samplers "Radiello" (F.S.Maugeri, Padova, Italy) and located 2,5 m above ground level and were placed in ninety representative sites in the studied area. Twenty volunteers were selected to evaluate the personal exposure and the samplers were exposed outside and inside their houses and each volunteer used portable passive monitors for two days.

Analysis of the diffusive samplers for VOC's was done by thermal desorption and gas chromatography with FID and NO₂ cartridges analysis were done by spectrophotometry of UV-Vis.

Ambient mean concentrations varied from 1,32 µg/m³ to 4,52 µg/m³ for the benzene, 7,24 µg/m³ to 26,37 µg/m³ for the toluene, 1,54 µg/m³ to 6,89 µg/m³ for the ethylbenzene, 4,05 µg/m³ to 37,1 µg/m³ for the m+p xylenes, 1,11 µg/m³ to 4,31 µg/m³ for o-xylene and 23 µg/m³ to 46,87 µg/m³ for the NO₂. The found levels depend on the climate, traffic density, gasoline composition and characteristics of the city.

Indoor/outdoor ratios were higher than 1 for all compounds, in some cases reaching a value of 2 or 3 and the indoor/personal ratios are lower than 1. These ratios give an approximation of the indoor air pollution and the exposure of people living in these houses.

The results obtained show that pollution inside the houses is greater than that in the air outside the houses and greater than the air in the city