

# The Diffusive Monitor

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## By way of Introduction

Welcome to the thirteenth edition of *The Diffusive Monitor*, which is a free publication of the Health and Safety Executive CAR Committee (Committee on Analytical Requirements), Working Group 5. This working group is concerned with workplace, indoor and environmental applications of diffusive sampling for assessing air quality.

The newsletter was started in May 1988 as a consequence of the Diffusive Sampling Symposium held in Luxembourg the previous year and is published approximately once a year. It contains articles on diffusive monitoring techniques and applications, and is a useful source of information on European and international standardisation in this area and of sampling rate data. Contributions are mostly from members of the Working Group, which has an international membership.

Contributions to the newsletter are not intended to be exclusively from HSE/CAR/WG 5, and any reader is welcome to submit a contribution for consideration. The only limitations are that articles should concentrate on diffusive sampling applications and should not be too obviously commercial.

The newsletter has a world circulation of some 200 people, all of whom have specifically requested the publication, so if you wish to contribute articles, you can be assured of a wide and receptive audience. Articles are not peer-reviewed, but are subject to the Editor's discretion.

Copies of the newsletter may be obtained from the Editor by registering at [richard.h.iacs.brown@hsl.gov.uk](mailto:richard.h.iacs.brown@hsl.gov.uk) (see page 17)

## CEN Air Quality Standards – An Update

An earlier article in *Diffusive Monitor* [1] explained the relationship between the standardisation activities of CEN/TC137 and TC264 and the then new European Directives on Air Quality, namely the Chemical Agents Directive (98/24/EC) [2] and the Ambient Air Directive (96/62/EC) [3].

### Workplace Atmospheres Standards

The task of developing appropriate standards for workplace air quality measurements within the European Community has been carried forward by Working Groups of the Comité Européen de Normalisation (CEN) Technical Committee TC 137.

As indicated in the earlier article, this TC has chosen not to develop specific measurement procedures, leaving this to the International Organisation for Standardisation (ISO), but to agree standards that specify the performance requirements that measurement methods should meet for them to be appropriate for implementing the Chemical Agents Directive. The main standard, EN 482 [4], specifies these requirements (principally that measurement uncertainty should be better than 30% in most cases), and specific standards elaborate the test methods for particular

devices or target compounds. Since 1997, further specific standards have been developed [5-10]. Standards for metals and metalloids, diesel particulate matter, dustiness, endotoxins, bioaerosol samplers and dermal sampling are also in progress.

### Ambient Air Standards

The task of developing appropriate standards for ambient air quality measurements within the European Community has been carried forward by Working Groups of CEN Technical Committee TC 264.

In the case of ambient air, however, the performance requirements are specified in the Directive(s), not in the CEN standards. Thus, although the 'framework' Directive [2] only gives general guidance on when and where to take measurements (or to use modelling or objective estimation), several associated Daughter Directives have been promulgated [11-12] or are under development. These Daughter Directives prescribe performance requirements as Data Quality Objectives (DQOs), including measurement uncertainty, minimum data capture and minimum time coverage.

These Daughter Directives are not entirely consistent in the definition of uncertainty (nor is this definition exactly the same as in EN 482). The 1999 Directive refers to "accuracy" as laid down in ISO GUM [13] or in ISO 5725-1 [14], whilst the 2000 Directive refers to the "uncertainty" (on a 95% confidence interval) in accordance with the principles of ISO GUM or the methodology of ISO 5725 or equivalent. The change of wording is probably the result of the realisation that the two ISO standards have different objectives. One, the ISO GUM is a guide for estimating uncertainties from a metrological point of view, whilst ISO 5725 is a practical implementation of a method evaluation procedure using an inter-laboratory test. An attempt to resolve the (apparent) inconsistency is given in the CEN TC264 document CR 14377 [15].

The primary task of CEN TC 264 is to recommend reference methods, where these are not already prescribed in Directives, and to evaluate them to determine if their performance meets the specified targets. These methods therefore contain the procedures for determining the measurement uncertainty (or its components) and either actual values determined by experiment or target values which if met by the user would meet the requirements specified in the (Daughter) Directives. In the specific case of diffusive samplers, which are likely to be used for indicative measurement, separate documents have been prepared [16,17] that contain the procedures for determining the measurement uncertainty.

For example, CEN/TC 264/WG 13 has a specific remit to develop the reference method(s) for benzene, in the context of the Directive on benzene and carbon monoxide [12]. The working group has decided to work on five standards [18-22], two of which are using diffusive sampling principles.

There is also the Daughter Directive on sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air [11]. Of these, sulphur dioxide, nitrogen dioxide and (potentially) oxides of nitrogen are amenable to diffusive monitoring, as well as CO from the benzene Directive, and WG11 is considering developing specific standards on these compounds. Ozone is also of interest in connection with Directive 2002/2/EC [23] and ammonia is of interest in connection with the Commission Proposal on national emission ceilings for certain atmospheric pollutants (1999).

1. R.H. Brown, *Diffusive Monitor*, 1998, **10**, 1-2.
2. Council Directive 98/24/EC on the protection of the health and safety of workers from the risks related to chemical agents at work (1998).
3. Council Directive 96/62/EC on ambient air quality assessment and management (1996).
4. Workplace atmospheres - General requirements for the performance of procedures for the measurement of chemical agents (EN 482:1994).
5. Workplace atmospheres - Requirements and test methods for pumps for sampling of

- chemical agents with a volume flow rate of over 5 l/min (EN 12919:1999).
6. Workplace atmospheres - Electrical apparatus used for the direct detection and direct concentration measurement of toxic gases and vapours. General requirements and test methods (EN 45544:1999).
7. Workplace atmospheres - Assessment of performance of instruments for measurement of airborne particles (EN 13205:2001).
8. Workplace atmospheres - Guidelines for measurement of airborne micro-organisms and endotoxin (EN 13098:2001).
9. Workplace atmospheres - Requirements and test methods for the measurement of chemical agents present as mixtures of aerosol and vapour (ENV 13936:2001).
10. Workplace atmospheres - Guide for the application and use of procedures and devices for the assessment of chemical and biological agents (EN 14042: at Final Vote).
11. Council Directive 99/30/EC relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air (1999).
12. Council Directive 2000/69/EC relating to limit values for benzene and carbon monoxide in ambient air (2000).
13. Guide to the Expression of Uncertainty of Measurements (ISO, 1993).
14. Accuracy (trueness and precision) of measurement methods and results (ISO 5725-1:1994).
15. Air Quality - Approach to uncertainty estimation for ambient air measurement methods (CEN CR 14377:2002)
16. Ambient Air Quality – Diffusive samplers for the determination of concentrations of gases and vapours – Requirements and test methods. Part 1: General requirements (EN 13528-1: at Final Vote).
17. Ambient Air Quality – Diffusive samplers for the determination of concentrations of gases and vapours – Requirements and test methods. Part 2: Specific requirements and test methods (EN 13528-2: at Final Vote).
18. Air Quality –Determination of benzene in ambient air by the capillary gas chromatography method – part 1: pumped sampling and thermal desorption. (WG 13 draft N 172).
19. Air Quality –Determination of benzene in ambient air by the capillary gas chromatography method – part 2: pumped sampling and solvent desorption. (WG 13 draft N 173).
20. Air Quality –Determination of benzene in ambient air by the capillary gas chromatography method – part 3: in situ measurements by automated gas chromatographic techniques. (WG 13 draft N 174).
21. Air Quality –Determination of benzene in ambient air by the capillary gas chromatography method – part 4: diffusive sampling and thermal desorption. (WG 13 draft N 175).
22. Air Quality –Determination of benzene in ambient air by the capillary gas chromatography method – part 5: diffusive sampling and solvent desorption. (WG 13 draft N 176).
23. Directive 2002/3/EC of the European Parliament and of the Council of 12 February 2002 relating to ozone in ambient air.

# A Multi-component Diffusive Sampler for Acidic Gases

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A diffusive sampler [1] that simultaneously samples different acidic gases such as: formic acid, acetic acid, hydrofluoric acid, hydrochloric acid and sulphur dioxide has been developed.

## Urban traffic measurements

Urban measurements were carried out in Stockholm, Sweden at a square used by buses using ethanol as fuel. The acetic acid concentrations measured were around 0.4 ppb.

## Measurements in museums

Recently the emissions from the interiors of museums and storage rooms have been considered to be an important factor in the deterioration of cultural and historical objects. Organic acids and aldehydes released from organic construction materials may be even more important than many of those gases linked to traffic and industrial exhaust transported into the buildings. The species normally monitored in the highest concentrations are formic and acetic acid, and formaldehyde that can be transformed into the more harmful formic acid. In a study made by the Swedish National Heritage Board, organic acids and aldehydes were monitored in six museums. Museums were selected to span from those having a good indoor climate to those assumed have poor conditions. Diffusive samplers were used with one month of exposure time. The concentrations of acetic acid varied from 0.2 to 58 ppb and from 0.2 to 46 ppb for formic acid. Objects not exposed at the museum are sometimes stored in drawers. Since diffusive samplers are small they can be placed inside drawers and display cases. When the sampled volume (uptake rate multiplied by exposure time) is close to or exceeds the volume of the drawer, the concentration can not be obtained, but the emission rate can. As an example, for a drawer volume of 26 litres, and sampled volume 1.5 m<sup>3</sup>, the emission rates of 54 µg/month of formic acid and 170 µg/month of acetic acid were obtained.

## Volcanic gas emissions

Volcanic gas emissions from active volcanoes are measured for three reasons; to increase our geo-scientific knowledge, for risk assessment and to study their environmental impact. Diffusive samplers were used in combination with other measurement techniques at Masaya volcano in Nicaragua during 15 April to 8 May 2001, with the purpose of assessing its applicability for semi-continuous monitoring of volcanic gases. This volcano is situated on a plateau at only about 600 m a.s.l., which implies that the concentrations can be very high at ground level and severe impact can be seen on surrounding vegetation within 30 km in the direction of the prevailing wind. Masaya had a minor explosion on the 23 April. The exposure times of the diffusive samplers varied from one hour to four days. The mixing ratios obtained varied; for HF from 2 to 600 ppb, for HCl from 3 ppb to 2.6 ppm and for SO<sub>2</sub> from 10 ppb to 7 ppm. On one occasion the stainless steel screen that protects the membrane in the sampler was completely corroded. This sorbent was over-exposed in this case so the concentration could not be estimated. The results demonstrate that diffusive samplers are a cost-effective way of gas monitoring on active volcanoes. Measurements should, however, be made at an appropriate distance from the crater to avoid saturation effects due to extreme exposures during short events.

### Acknowledgment

Financial support has been gratefully received from King Carl the XVIth Gustaf's 50th anniversary foundation.

*A fuller description of the work on volcanic gas emissions is given in ref 1.*

1. Allen A. G., Oppenheimer C., Ferm M., Baxter P. J., Horrocks L. A., Galle B., McGonigle A. J. S., and Duffell H. J. (2002) Primary sulphate aerosol and associated emissions from Masaya volcano, Nicaragua. *J. Geophys. Res.* (accepted for publication).

## Diffusive Sampling for the Assessment of Air Quality in Museums

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### Introduction

There is a general consensus among conservators that atmospheric pollutants can be a threat to the cultural heritage in Museums [1,2]. A variety of gas-phase pollutants found indoors can cause corrosion and damage to works of art.

SO<sub>2</sub> was one of the first air pollutants recognised as harmful to artworks. Additional concerns have been raised beginning at the end of the 1980's regarding the effects of nitrogen compounds indoors. Nitrogen chemistry has been shown to have the potential to create indoor nitrous and nitric acid [2, 3]. Another molecule which is aggressive to pigments and to organic materials is ozone. Alizarin-based lakes and yellow pigments in watercolours were found to be particularly sensitive to this pollutant [4].

The European Union, through the DGXII (research), has become involved in channelling the efforts of many research groups in the field of the protection of artworks and the need to monitor atmospheric concentration of the mentioned pollutants is now perceived to be an important component of preventive conservation in Museums. Diffusive sampling can be adopted to analyse in detail the temporal and spatial trends of pollutants concentration in museums. Compared with conventional sampling they have many clear advantages. These include low cost, no requirement for power supply, simplicity of deployment and use. They can be used virtually anywhere and they can be deployed in large numbers to provide detailed spatial and temporal surveys.

In this work we present the results of an ongoing monitoring activity based on the use of a recently developed diffusion-

based sampler in three different rooms of the Uffizi Gallery and concomitant outdoor measurements.

**Experimental**

The sampling campaign at the Uffizi Gallery (Florence) was carried out by monitoring ozone, sulphur dioxide, nitrogen dioxide, nitrogen oxides, nitrous and nitric acids for eight periods from March 2001 to February 2002. Three rooms were chosen (rooms no. 9, 15 and 20). The monitoring device used in this study was a diffusion sampler patented by CNR under the name Analyst<sup>®</sup> (Marbaglass, Rome, Italy). For all the monitored species (with the exception of NO<sub>x</sub> and O<sub>3</sub>) the body of the sampler is a cylindrical glass vial with a threaded cap at one end (Figure 1a). The pollutant is collected on an impregnated disc placed at the bottom of the device and held in position by a stainless steel ring.

A slightly different design was adopted to monitor ozone which is collected on a nitrite-impregnated fibreglass disk placed on a polyethylene disc having three small bulges that supports the collecting filter (Figure 1b). For NO<sub>x</sub>, the absorbing pad is placed in front of an oxidant surface, placed at the bottom of the vial, which is able to convert NO to NO<sub>2</sub>. The reliability of this device has been demonstrated in a number of laboratory and field studies. Reference is made to papers 5-10 for details on the samplers used.

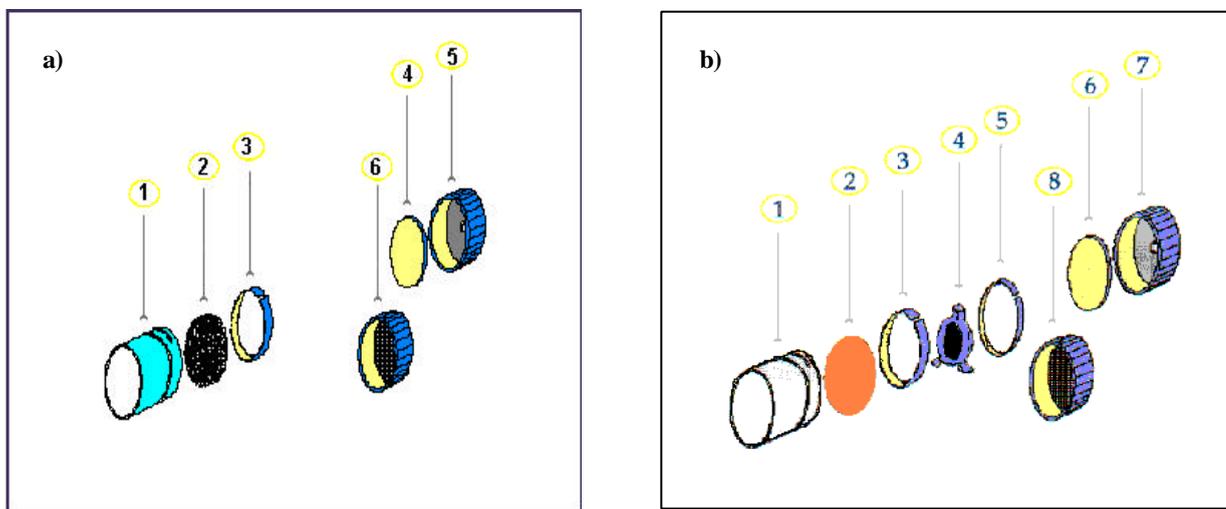


Fig 1: Exploded schemes of Analyst<sup>®</sup> passive samplers. a) Analyst<sup>®</sup> for NO<sub>2</sub>, SO<sub>2</sub>, HNO<sub>2</sub> and HNO<sub>3</sub>: 1 – glass cylinder; 2 – absorbent pad; 3 – ring; 4 septum; 5 – plastic cap; 6 – air barrier. b) Analyst<sup>®</sup> for NO<sub>x</sub> and O<sub>3</sub>: 1 – glass cylinder; 2 – NO<sub>x</sub> oxidant (does not apply for O<sub>3</sub> sampler); 3 – ring; 4 – absorbent pad; 5 – ring; 6 – septum; 7 – plastic cap; 8 – air barrier.

**Results and Discussion**

Figure 2 shows the Indoor/Outdoor concentration ratios in the selected rooms for the six pollutants monitored. I/O ratios are often used as indicators of the relative contribution from indoor and outdoor sources to the indoor exposure to

air pollution. Obviously, this approach cannot distinguish between indoor and outdoor sources. In the present case, however, I/O ratios are good indicators of both penetration from outdoors and reactivity for a given species. SO<sub>2</sub>, O<sub>3</sub> and HNO<sub>3</sub> were, as expected from their reactivity, invariably lower indoors whereas indoor NO<sub>x</sub> and NO<sub>2</sub> in

the majority of the cases studied were similar to the corresponding outdoor values. The relationship between indoor and outdoor levels of SO<sub>2</sub> was also measured by Hackney [1] and typical indoor/outdoor ratios for O<sub>3</sub> and SO<sub>2</sub> measured in a number of museums, as reviewed by Brimblecombe [2], are of the same order of the values measured here. Surface area to volume ratios play a significant role in determining how much outdoor ozone is introduced into the room and for what period of time it

persists inside the room. The rooms with higher surface-area-to-volume ratios tend to have higher decay rates for ozone. Apparently, SO<sub>2</sub> is less sensible to this parameter. It is clear that the I/O ratio may be affected by certain other factors such as the reactivity of surface material (i.e. the quality and nature of plaster) and relative humidity. As expected on the basis of previous studies [3], indoor HNO<sub>2</sub> levels were found to largely exceed that outdoors.

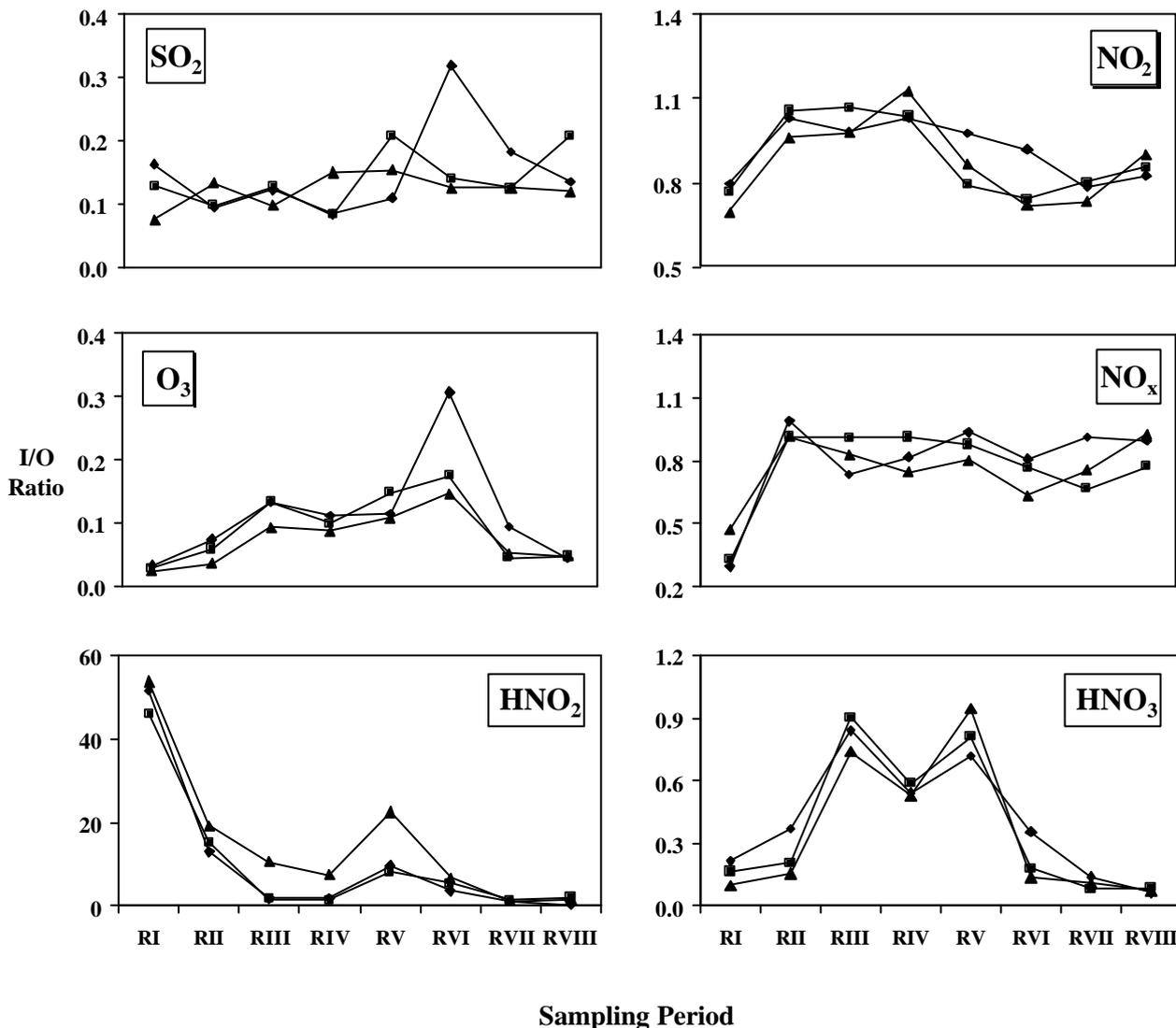


FIG 2: Indoor/Outdoor average concentration ratios (I/O) for SO<sub>2</sub>, O<sub>3</sub>, NO<sub>x</sub>, HNO<sub>2</sub>, NO<sub>2</sub> and HNO<sub>3</sub> measured during the eight sampling runs (RI – RVIII) in the three rooms at the Uffizi Gallery, Florence [◆ Pollaiolo’s room (#9); ■ Leonardo’s room (#15); ▲ Dürer’s room (#20)].

The concentration-time behaviour is supportive of a formation of nitrous acid indoors, formed via reaction of NO<sub>2</sub> with water on surfaces. Since indoor environments are characterised by high surface-to-volume ratios in

comparison to those outdoor, the formation of HNO<sub>2</sub> is highly favoured in these conditions. In addition, given the absence of sunlight, photolysis is less important indoors. Examination of the graphs for HNO<sub>2</sub> and O<sub>3</sub> of Figure 2 suggests that indoor HNO<sub>2</sub> is not present in significant

amount when indoor O<sub>3</sub> concentrations are high. A probable explanation involves the interaction of gaseous ozone and nitrite in the aqueous surface film formed by reaction of NO<sub>2</sub> with water on walls.

It can be expected that the decay parameter for the most reactive species will play a role. A remarkable difference between NO<sub>x</sub> and the most reactive pollutants such as SO<sub>2</sub> and O<sub>3</sub> is that for NO<sub>x</sub> the pattern in the indoor concentrations mirrors that of the outdoor concentration. The patterns for HNO<sub>2</sub> and HNO<sub>3</sub> are more difficult to interpret because for both species the interplay between formation (from NO<sub>2</sub>) and reactivity (e.g. deposition to walls) is particularly complex, when using data averaged over such a long period. Mean nitric acid (HNO<sub>3</sub>) indoor concentration varied from 0.7 to 12.2 µg/m<sup>3</sup>. The trend for this species is apparently anti-correlated to the trend for HNO<sub>2</sub>. Furthermore, as it can be seen in Figure 2, in the central part of the monitoring campaign high I/O ratios from HNO<sub>3</sub> were measured.

## Conclusions

Diffusive samplers can be used to check the effectiveness of any air-conditioning and filtering system installed to protect works of art.

Diffusive samplers are an ideal tool for determining the pollutants distribution in more than one room simultaneously in comparison to outdoor concentrations. They are useful to assess integrated concentration levels over long period of time.

The main advantage of these sampling devices is that they are inexpensive and easy to use. Compared with the pump-dependent active sampling procedure (i.e. diffusion denuders or automatic analysers), the main advantages of the method are cost effectiveness and simplicity.

## Acknowledgements

Financial assistance from EC DG XII (project "MIMIC") and technical assistance from the staff of the Uffizi Gallery are gratefully acknowledged.

1. S. Hackney, *Stud. Conserv.*, **29**, 105-116 (1984).
2. P. Brimblecombe, *Atm. Environ.*, **24B**, 1-18 (1990).
3. F. De Santis, V. Di Palo and I. Allegrini, *Sci. Total Environ.*, **127**, 211-223 (1992).
4. C.L. Shaver, G.R. Cass and J.R. Druzik, *Environ. Sci Technol.*, **17**, 748-752 (1983).
5. F. De Santis, T. Dogeroglu, A. Fino, C. Vazzana and I. Allegrini, *Proceedings of the Congress "Terzo Millennio"* Rome - Italy, 22-24 February 2000, 27.
6. F. De Santis, A. Fino, C. Vazzana and I. Allegrini, *Proceedings of the Conference "La Chimica e l'Arte"*, Bressanone - Italy, 26th February - 1st March 2000, 33.
7. F. De Santis, A. Fino, C. Vazzana and I. Allegrini, *Proceedings of the Conference "Euroanalysis XI"*, Lisbon - Portugal, 3-9 September 2000, OC62.
8. F. De Santis, T. Dogeroglu, S. Menichelli, C. Vazzana and I. Allegrini, *The Scientific World*, **1**, 475-482 (2001).
9. F. De Santis, I. Allegrini, T. Dogeroglu, S. Menichelli and C. Vazzana, *Proceedings of the International Conference "Measuring Air Pollutants by Diffusive Sampling"*, Montpellier - France, 26-28 September 2001, in press.

10. F. De Santis, T. Dogeroglu, A. Fino, S. Menichelli, C. Vazzana and I. Allegrini, *Anal. Bioanal. Chem.*, in press.

## Blanks on Carbograph-4

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The use of 'blanks' is a typical QA/QC procedure in most analytical methods where sampling on adsorbents is required. This is mainly due to the fact that adsorbents can frequently be contaminated during storage or transport. The analyst must be sure that the possible contamination of the adsorbent, or changes in the original composition (losses during storage), are due to factors that can be minimised by quality control.

The first step is to guarantee a clean adsorbent before sampling. The manufacturing of adsorbents (presence of by-products as possible interferences), their post-purification and conditioning are critical stages in the success of the procurement of a right adsorbent. Secondly, in the case of the thermal desorption technique, the use of stable adsorbents at working temperature and with time, i.e., no degradation of the adsorbent material during storage, is a must. The genesis of 'artifacts' is not always well understood. The presence of 'by-products', i.e. impurities of the reagents used during manufacture, may explain the generation of aldehydes and ketones that appear in Tenax [1]. This also happens when Tenax is exposed to ozone or other reactive species; the presence during sampling of unsaturated compounds – terpenes – can result in the formation of artifacts [2]. Another possibility is the degradation of the analytes on the surface of the adsorbents: this was the case for α- or β-pinene adsorbed on Carbotrap or Chromosorb 106 [3]. The presence of surface oxides on carbon molecular sieves such as Carbosieve or Carboxen explained the instability observed for 1,3-butadiene and isoprene on these adsorbents [4].

The main restriction when significant blanks are present in the adsorbent is the increase of the limit of quantification of the analytes. It, thus, becomes impossible to analyse accurately low concentration levels or, for instance, to use diffusive sampling for short exposure periods.

The use of stronger adsorbents, which prevent back diffusion during diffusive sampling, implies the use of higher desorption temperatures that can also produce higher blank levels. This effect was observed for Carbograph-4 when blank levels of aromatic hydrocarbons from three different laboratories, which were using different desorption temperatures for analysis, were compared (Table 1).

Table 1: Blank levels (ng) of aromatic hydrocarbons on Carbograph-4: different desorption temperatures

LABORATORY			Benzene	Toluene	Ethyl-benzene	m-xylene
A	blanks 14	Positives	6	6	5	2
		Average	14.8	27.8	14.5	22.9
		St dev	5.7	21.9	7.7	18.7
B	blanks 18	Positives	6	16	13	14
		Average	17.4	41.3	11.2	27.4
		St dev	5.4	27.8	3.1	19.5
C	blanks 16	Positives	9	9	7	3
		Average	40.7	34.6	18.0	15.3
		St dev	23.6	29.5	9.0	12.0

Positives: number of blanks over the detection limit.

The tubes were conditioned for field campaigns by following similar procedures (1 hour at 350 C and a nitrogen flow of about 100 ml/min). Nevertheless, the desorption temperature during analysis was different: Laboratories A and B used 320 C for 10 min and laboratory C used 350 C for 5 min.

Additionally, a series of tubes preloaded with about 200 ng of BTEX were cleaned, under different temperature conditions (375 and 350 C), for 1 hour with a nitrogen flow of about 100 ml/min. Afterwards, tubes from these batches were desorbed for analysis at 320 C for 10 mins and 350 C for 5 mins. Results are given in Table 2.

Table 2: Blank levels (ng) of aromatic hydrocarbons on Carbograph-4: different conditioning and desorption temperatures

	Benzene	Toluene	m-Xylene	o-Xylene
Cleaned at 375 C for 1 hour 100 ml/min Analysed at 350 C for 5 min	19.13	7.39	6.16	3.36
	9.80	4.55	3.91	1.40
	27.62	11.47	7.79	5.59
	13.47	3.77	2.48	1.53
Cleaned at 350 C for 1 hour 100 ml/min Analysed at 350 C for 5 min	5.87	3.63	2.84	2.96
	4.38	1.76	n.d.	n.d.
	4.88	2.01	n.d.	n.d.
	3.96	1.81	n.d.	2.77
Cleaned at 350 C for 1 hour 100 ml/min Analysed at 320 C for 10 min	2.33	1.83	n.d.	n.d.
	2.57	1.00	n.d.	n.d.
	1.89	1.02	n.d.	n.d.
	1.24	1.12	n.d.	n.d.

n.d.: not detected

In the light of these results, it is possible to expect an increase in the blank levels the higher the desorption or conditioning temperature are; this being of particular importance for temperatures higher than 350 C.

A full series of experiments in order to study adsorbates' stability in Carbograph-4 has not been carried out yet. Nevertheless, the appearance of benzaldehyde, acetophenone and 4-methylbenzaldehyde in tubes exposed

to a mixture of BTEX and stored at ambient temperature was observed. These compounds were also observed in samplers exposed for 5 days to ambient air and analysed directly without storage.

To check the possible oxidation of these compounds in Carbograph-4, loaded tubes with about 30 ng of BTX were flushed with one litre of air containing 200 ppb of ozone. The tubes were analysed and compared with non-flushed tubes. The results showed no effect on the loaded amount of benzene. Nevertheless, toluene and m-xylene showed a slight decrease in concentration. In parallel, new peaks appeared in the chromatogram where it was possible to identify benzaldehyde, 4-methylbenzaldehyde and acetophenone.

In conclusion, the use of Carbograph-4 for ambient air sampling needs to be carefully evaluated. The preparation and conditioning of the adsorbent appear to be a critical factor in the performance of the adsorbent. Furthermore, reactions at the surface of the adsorbent seem to be catalysed when oxidants or other reactive agents are present.

1. Cao, X-L and Hewitt, N.C. Chemosphere (1993), 695-705.
2. Cao, X-L and Hewitt, N.C. Environ. Sci. Technol. (1994), 28, 5, 757-762.
3. Dettmer, K; Knobloch, Th., Engewald, W. Fresenius J Anal. Chem (2000), 366:70-78.
4. Helming, D.; Greenberg, J.P. (1994), J. Chromatogr. 677: 123-132.

## A New Exposure Chamber for the Determination of Diffusive Sampler Performance

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### Introduction

The assessment of ambient air quality by diffusive samplers, has been expanding continuously especially after the publication of the EC Air Quality Framework Directive. Diffusive samplers can be seen today as cost effective, sensitive and reliable tools for the assessment of personal exposure and air quality in both indoor and outdoor environments.

Standardisation groups CEN/TC 264 WG11 and WG13 have been working on two important standards [1,2]. These standards should provide the user of diffusive samplers with guidance and standardised procedures to make the best possible use of these devices.

Part 3 of the EN 13528 standard specifies that, though the performance of a diffusive sampler can be determined theoretically, it is good practice to determine this experimentally in an exposure chamber, where environmental conditions typical of the sampler's intended use can be reproduced.

Exposure chambers should be able to:

- Accommodate at least 12 samplers
- Produce a continuous reference atmosphere for a duration up to several weeks
- Simulate variable wind speeds
- Vary humidity and temperature
- Provide equal loading conditions for all samplers being exposed.

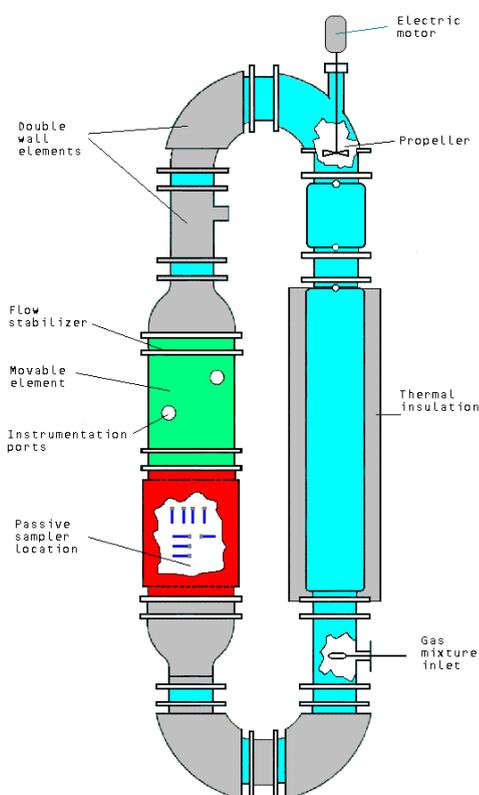


Fig 1: INERIS Exposure Chamber  
**INERIS Development**

An exposure chamber has been developed at INERIS for the determination of diffusive sampler performance. See fig. 1.

Basically, it consists in a loop made of glass, stainless steel and PTFE containing the reference atmosphere where diffusive samplers are exposed.

The main characteristics of the chamber are:

*Dimensions:*

- Exposure zone D= 300mm, h= 700mm
- Overall high H= 2.5m
- Total weight W= 450 kg (approx.)

*Supports:*

The chamber has been installed vertically and is supported by a soldered steel frame. There is a movable section that can swing; giving access to the exposure area. This movable section is held by an oscillating arm fitted with a preloaded spring. This mechanical arrangement facilitates the opening of the chamber for the introduction or the removal of the samplers. These samplers are attached to a basket made of stainless steel

*Gas mixtures:*

The contaminated atmosphere for the exposure is prepared separately by continuous dilution of a more concentrated mixture. This dilution is performed with the help of mass flow meters. Humidity is added by passing part of the dilution gas through a bath of HPLC quality water maintained at constant temperature.

Typical concentrations of gas mixtures are in the ppb range; theoretically however, any level of concentration can be reproduced.

The diluted gas mixture is introduced into the chamber at a flow rate of one to several litres per minute in order to replace the total volume of the chamber (150L) several times a day and to insure that the mixture concentration downstream of the exposure area is not significantly depleted. This is particularly important when exposing samplers that have high uptake rates.

*Wind speed:*

The exposure conditions for the samplers should be such that turbulent diffusion inside the sampler air gap is prevented or minimised. This “wind effect”, can be controlled by adjusting the speed of a “model aeroplane” propeller located inside the chamber. Since the flow path is not straight, there is an undesirable jet effect up-stream of the exposure zone. This difficulty has been overcome using a flow stabiliser. This device is a drilled polished stainless steel plate. Downstream this plate, the flow is still turbulent but all samplers are exposed to similar wind conditions.

*Temperature:*

One of the most attractive features of this chamber is the possibility to work within a wide range of temperatures, typically from -10°C to +50°C. This can be achieved by the use of double wall elements made of glass. A fluid is heated or cooled down in an external conditioner and drawn through the double walls of the entire device. The necessary

thermal insulation is composed of 52 special jackets made of polyurethane foam, PTFE and aluminium.

#### Monitoring:

All working parameters are continuously monitored:

Temperatures, by Pt 100 probes.

Humidity, by a capacity probe (Hanna Instruments HI 916010 C).

Wind speed, by Annubar type probe (Diamond II, Dielerich Standard USA).

Total pressure, by an electronic manometer (Furness Ltd.).

Gas mixture flow rate, by mass flow meters (Tylan type).

Gas mixture composition: variable depending on the compounds of interest e.g. Automatic GC+FID for hydrocarbons, Chem. Lum. Monitor for NO<sub>2</sub>, etc.

#### Validation Test

Several Perkin-Elmer type samplers (RPE) packed with Carbotrap B have been tested under the following conditions:

Number of samplers n=9

Type: RPE Carbotrap B

Temperature: 20°C

Humidity: 50 %

Pressure: 1 atm.

Duration: 5.7 days

Concentration: 4.19 µg/m<sup>3</sup> benzene in synthetic air

After thermal desorption of the samplers and analysis of the benzene sampled during the exposure, uptake rates were calculated. Results are presented in Table 1

Table 1. RPE tubes exposed to a concentration of 4.19 µg/m<sup>3</sup>. Zero of the chamber <1 µg/m<sup>3</sup>

Tube number	Position in the chamber	Uptake rate ml/min
A60829	7V top	0.42
A60699	4H middle	0.42
A49068	3V top	0.43
A56116	2H bottom	0.43
A57629	4V top	0.43
A47625	5V top	0.41
A31749	7 H middle	0.44
A73374	6 V middle	0.41
A35691	1 V top	0.41
	<b>Average (SD%)</b>	<b>0.42 ( 2.9 )</b>

*V and H stand for vertical and horizontal respectively*

The values of the uptake rates obtained in this experiment have been compared with those deduced from another test carried out with the same samplers under the same conditions using the NPL facility in the UK [3]. The difference observed on the average was 12.5%

#### Conclusions:

The low relative standard deviation observed (2.9%), shows that samplers were exposed to very similar conditions in the exposure area. Thanks to the technical solutions adopted for its design, this chamber allows the determination of diffusive sampler performance in a wide range of experimental conditions in compliance with the new standards for the monitoring of ambient air by diffusive means.

#### Acknowledgements

The author wishes to thank Armelle Frezier, Nathalie François and Jean-Claude Pinard for their technical assistance.

1. European standard EN 13528-2 Ambient Air Quality. Diffusive samplers for the determination of concentration of gases and vapours. Specific requirements and test methods.
2. European Standard. (in preparation) Air Quality - Determination of benzene in ambient air by the capillary gas chromatography method - Part 4: Diffusive sampling and thermal desorption.
1. Evaluation des performances des préleveurs par diffusion pour l'analyse des BTX à l'air ambiant. Rapport INERIS, December 2001.

## Determination of the Benzene Diffusive Uptake Rate for the sorbent Carbopack X employed in Perkin Elmer type samplers

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#### Introduction

This article presents validation work carried out for the first time on Carbopack X, a substance that is intermediate between graphitised carbon and molecular sieve. Perkin Elmer type diffusive samplers filled with this sorbent were dosed in the National Physical Laboratory's Controlled Atmosphere Test Facility (CATFAC). The two-week benzene uptake rate was measured over a range of concentrations and environmental conditions.

#### Experimental

A detailed description of the CATFAC has already appeared elsewhere [1]. Very briefly, traceable atmospheres of benzene (and benzene, toluene and o-xylene (BTX)) were generated at a constant temperature, relative humidity and a wind speed of 0.5 m s<sup>-1</sup>. Continuous on-line monitoring of the hydrocarbon concentration in the CATFAC was

performed by gas chromatography, where gas samples were automatically extracted into a pre-concentrator coupled to a gas chromatograph (GC). Calibration of the concentration of species was achieved by injecting similar sample volumes of NPL multi-component gravimetric "BTX" hydrocarbon primary gas standards into the GC. These traceable standards are regularly intercompared with those of other National Standards Laboratories worldwide to demonstrate their accuracy.

After sampling the atmosphere for two-weeks in the CATFAC, the Perkin Elmer type diffusive samplers were sealed and analysed with unexposed samplers, which had been retained as travelling blanks. The analysis used the technique of thermal desorption, followed by detection with gas chromatography, and was performed in accordance with established procedures [2]. Traceable gravimetric VOC liquid standards were employed for the calibration, which are intercompared through the Workplace Analysis Scheme for Proficiency (WASP) run by the Health and Safety Laboratory, UK.

Early experiments carried out on tubes filled with Carbopack X showed that the typical desorption efficiency for benzene

was 100%. Typical blank values for benzene were found to be  $(1.70 \pm 0.15)$  ng tube<sup>-1</sup>. With storage over 12 weeks, the mass of benzene in the blanks increased to  $(2.48 \pm 0.27)$  ng tube<sup>-1</sup>.

## Results and Discussion

Fick's 1<sup>st</sup> Law of Diffusion describes the uptake of each component, for a given sorbent. For Perkin Elmer type devices the concentration is given by:

$$C' = m/U_p . t \quad (1)$$

where:

$C'$  is the concentration (ppm),

$m$  is the amount of substance on the tube (ng),

$t$  is the time (min) and

$U_p$  is the uptake rate (ng ppm<sup>-1</sup> min<sup>-1</sup>) for each hydrocarbon, using a defined sorbent.

A summary of the measured uptake rates obtained using this equation is given in Table 1.

Table 1: Measured two week diffusive uptake rate data for Carbopack X.

Date of measurement	Measured uptake rate, ng ppm <sup>-1</sup> min <sup>-1</sup>			CATFAC concentrations, ppb			R H, %	Temperature, °C	No of diffusive samplers
	benzene	toluene	o-xylene	benzene	toluene	o-xylene			
Feb-01	1.89 ± 0.43			1.55 ± 0.04			45 ± 7	10 ± 2	9
Mar - Apr 01	1.97 ± 0.44			1.54 ± 0.05			50 ± 7	32 ± 2	9
Aug-01	1.91 ± 0.43	2.23 ± 0.52	1.79 ± 0.41	5.45 ± 0.11	16.6 ± 0.34	5.18 ± 0.11	50 ± 5	20 ± 1	32
09/01 - 12/01	2.14 ± 0.48			1.45 ± 0.04			50 ± 5	20 ± 1	9
09/01 - 12/01	1.93 ± 0.43			7.68 ± 0.19			50 ± 5	20 ± 1	9
09/01 - 12/01	2.12 ± 0.52			0.17 ± 0.01			50 ± 5	20 ± 1	9
09/01 - 12/01	1.00 ± 0.37			1.77 ± 0.05			90 ± 5	20 ± 1	9

Within the experimental uncertainty the benzene two-week uptake rate for Carbopack X appeared to be invariant with concentration for the measurements carried out at 20 °C and around 50% relative humidity. This was the case for the wide benzene concentration range of  $(0.17 \pm 0.01)$  ppb to  $(7.68 \pm 0.19)$  ppb, and also for the multi-component atmosphere of benzene, toluene and o-xylene. Further studies undertaken at 10 °C and 32 °C showed similar results to those obtained at 20 °C. A two-tailed Student t-test was applied to six sets of the data. At the 95% confidence level, no significant difference was found for all possible combinations. It is only at 90 % relative humidity that any falloff in the uptake rate was observed, down to  $(1.00 \pm 0.37)$  ng ppm<sup>-1</sup> min<sup>-1</sup>.

## Conclusions

The two-week benzene diffusive uptake rate for Carbopack X (together with a more limited set for toluene and o-xylene) for environmental applications has been measured for the first time at 10°C, 20°C and 32°C, over a wide range of benzene (and toluene and o-xylene) concentrations, at a wind speed of 0.5 m s<sup>-1</sup> and mainly 50% relative humidity. From the six separate determinations at around 50% relative humidity, the mean benzene uptake rate was found to be  $(1.99 \pm 0.18)$  ng ppm<sup>-1</sup> min<sup>-1</sup>. All the uncertainties quoted refer to standard uncertainties multiplied by a coverage factor of two, giving a level of confidence of approximately 95%.

### Acknowledgements

We gratefully acknowledge the support received from the Valid Analytical Measurement (VAM) Programme of the UK Department of Trade and Industry, and the European Union through Technical Committee 264 of Working Group 13 of the Comité Européen de Normalisation (CEN).

1. Martin, N. A., Dedman, S. A., Gough S. C., Henderson, M. H., and Goody, B. A., 2001. An international facility for the validation of diffusive and pumped samplers. *Valid Analytical Measurement Bulletin*. Issue 25 (August) 10-13.
2. Health and Safety Executive, 1995. Volatile organic compounds in air. Laboratory method using diffusive solid sorbent tubes, thermal desorption and gas chromatography. Method MDHS 80.

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## The BRE study of indoor air quality in English homes

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### Introduction

BRE has conducted a national survey of air pollutants in 876 homes in England. Some data on indoor pollutants in English homes are available from previous studies (e.g. [1-4]). Although these studies provided valuable information, it could not be assumed that the homes studied were typical of homes across England as a whole. Therefore, the survey reported here was carried out to obtain more representative data, to increase knowledge of pollutant levels and the factors associated with high concentrations. Full details of the study have been published in two BRE reports [5,6].

### Method

Pollutants were monitored once in each home, using diffusive samplers, as follows:

Carbon monoxide (CO): Dräger colorimetric diffusion tubes, 14-day time-weighted average (TWA) in the kitchen and main bedroom.

Nitrogen dioxide (NO<sub>2</sub>): Palmes diffusion tubes, 14-day TWA in kitchens, main bedrooms and outside the homes.

Formaldehyde (HCHO): GMD 570 series dosimeter, three-day TWA in the bedroom.

Volatile organic compounds (VOCs): stainless steel sampling tubes packed with Tenax TA, four-week TWA in

the bedroom – reported as total VOCs (TVOC) and 22 individual VOCs.

Also, in each household an interviewer administered a questionnaire about the characteristics of the home, the occupiers and their activities. The interviewer also demonstrated the use of the various diffusive air samplers and agreed a suitable location with the householder. The samplers were subsequently sent to the householder by post, together with instructions for their use, self-completion questionnaires about activities during the sampling time and reply-paid envelopes for the return of the samplers and questionnaires to BRE.

### Results

Minimum, maximum, geometric mean and percentile values for some of the pollutants are shown in Table 1.

Concentrations of CO were higher in kitchens than in bedrooms, but significantly correlated. Higher levels of CO were found in autumn and winter, in urban areas, in homes with a gas oven, homes with unflued fossil fuel heaters, and in smokers' homes. The CO concentration did not exceed the WHO 8-hour average guideline value in any home.

Outdoor NO<sub>2</sub> concentrations were higher in autumn/winter and in urban areas. Kitchen levels were higher than outdoor levels in homes with gas cooking. Bedroom levels were lower than outdoors due to sink effects. Indoor NO<sub>2</sub> levels were highest in urban homes, older homes, terraced houses, homes with gas cooking and smokers' homes. Seasonal variation in indoor levels resulted mainly from indoor sources, rather than outdoor variations. The WHO air quality guideline for annual exposure to NO<sub>2</sub> was exceeded in more than 50% of kitchens that had a gas oven.

HCHO concentrations were higher in newer homes (increasing from 1940 onwards); in homes with a particleboard floor, especially a particleboard floor in the room where the sampling took place; and in summer and autumn than in winter or spring. The mean concentrations were well within the WHO air quality guideline, but the guideline was exceeded in six homes (0.7% of the total), of which five were under three years old.

Important factors for TVOC and/or one or more individual VOCs include dwelling age, season, building location (urban or rural), having an integral or attached garage, vehicle fuel, smoking, use of toiletries and painting and decorating. TVOC levels in 5% of homes exceeded 1000 µg m<sup>-3</sup>. The current EU target for benzene in outdoor air [7] was exceeded in 4.3% of homes, and 0.7% exceeded the WHO [8]1-week guideline for toluene.

Table 1. Statistics for pollutant concentrations ( $\mu\text{g m}^{-3}$ )

Pollutant	Location	Minimum	Maximum	Geometric mean	Percentiles			
					10%	50%	75%	95%
CO	Kitchen	<0.01	4.45	0.47	140	500	900	2070
	Bedroom	<0.01	3.90	0.39	120	440	690	1680
NO <sub>2</sub>	Kitchen	0.8	620.0	21.8	7.2	21.8	40.1	90.0
	Bedroom	0.4	752.6	11.9	4.4	12.1	19.8	38.1
	Outdoors	1.0	151.6	20.9	9.9	22.5	32.4	48.9
HCHO	Bedroom	1	171	22.2	9.8	24.0	35.2	61.2
TVOC	Bedroom	15	3360	210	72	202	352	1010
Benzene	Bedroom	<0.1	93.5	3.0	1.0	3.3	5.8	14.6
Toluene	Bedroom	0.3	1783.5	15.1	4.4	14.9	27.9	74.9
M/p-xylene	Bedroom	0.1	152.8	3.8	0.9	3.7	7.5	30.3
Limonene	Bedroom	<0.1	308.4	6.2	1.3	7.1	15.5	51.0
Undecane	Bedroom	<0.1	246.6	2.6	0.5	2.3	5.5	33.6

## Conclusions

The survey successfully applied diffusive samplers to identify factors influencing pollutant concentrations in UK homes. It is notable that seasonal effects on CO and NO<sub>2</sub> were due largely to indoor sources; this would need to be considered when interpreting time series studies of the effect of outdoor air pollution on health. Average levels of NO<sub>2</sub> in the kitchens of more than 50% of homes in England that have a gas oven exceed the WHO air quality guideline for annual exposure to NO<sub>2</sub> and the health implications of this exposure deserve further investigation.

Formaldehyde and VOC levels are highest in very new homes, and may breach the WHO guideline level, which has implications for regulation of emissions from materials and for ventilation requirements in new homes.

### Acknowledgements

This work was funded by the Chemicals and Biotechnology Division of the Department of the Environment, Transport and the Regions.

- Berry RW, Brown VM, Coward SKD, et al (1996) *Indoor Air Quality in Homes: The BRE Indoor Environment Study, Parts 1 and 2*. BRE Reports BR299 and BR300. London: CRC.
- Wiech CR & Raw GJ (1995) Asthma, dust mites, ventilation and air quality: study design and initial carbon monoxide results, *Proceedings of Healthy Buildings 95*, Milan, Vol 1. pp425-430.
- Wiech CR & Raw GJ (1996) The effect of mechanical ventilation on indoor nitrogen dioxide levels, *Proceedings of Indoor Air '96*, Vol 2, pp123 – 128. Nagoya: Indoor Air '96.
- Venn A, Antoniak M, Cooper M et al (2001) Common indoor air pollutants in the home and the risk and severity of wheezing illness in schoolchildren. *Am. J. Respiratory Critical Care Medicine*. Vol. 163, A722.
- Coward SKD, Llewellyn JW, Raw GJ et al (2001) *Indoor Air Quality in Homes in England*. BRE Report 433. London: CRC.
- Coward SKD, Brown VM, Crump DR et al (2002). *Indoor Air Quality in Homes in England – Volatile Organic Compounds* BRE Report 446, London: CRC.
- DEFRA (2001) *The Air Quality Strategy for England, Scotland, Wales and Northern Ireland – a consultation document on proposals for air quality objectives for particles, benzene, carbon monoxide and PAHs*. Department for Environment, Food & Rural Affairs, London.

- World Health Organisation (2000) *Guidelines for Air Quality*. Geneva: WHO.

## Novel Uses of Diffusive Monitors (examples from the BP Network)

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This article describes uses of diffusive monitors within some of the BP locations in UK and Europe. Examples of workplace and ambient air applications are given.

### A Brief History of Use within BP

One of the earlier and higher profile applications of diffusive monitors (DMs) to investigate ambient air quality was undertaken at the BP Chemicals Baglan Bay Site around 1990/91. At similar times programs were begun at other UK sites in Grangemouth and Hull. Some of these programs have changed as time and events have progressed, but substantial use of this technique is still made both in UK and European locations. DM applications have also been widely applied within the workplace as part of exposure studies to support chemical risk assessments. A recent internal questionnaire suggested that as much as 80% of thermal desorption analysis (typically using Perkin Elmer tubes with ATD400 equipment for exposure applications) made use of diffusive techniques, as opposed to pumped sampling methods. It is clear that DMs are being applied to many current occupational hygiene issues as well as to ambient air measurements.

## Environmental Applications

An example of a current diffusive monitoring program to help understand local air quality issues and impact can be found at the BP Hull Chemical Site. The program, developed in 1992, is still very active and now includes 9 perimeter stations around the site and 4 in local villages (up to 3 km distance). Initially, duplicate diffusive monitors were positioned at each station and collected on a 14-day basis (using DMs with Tenax GR adsorbent); but this changed to a 28-day frequency in 1999 (and now uses Carbpak B adsorbent). The data is processed in a number of ways but in its simplest form uses a standardised uptake rate to give a simple summed VOC response. The next level of investigation involves identification, quantification and trending (by correction for individual uptake rates, where appropriate, of specific components). Primarily this is done to allow a comparison of one station with another to help identify those with greatest VOC contributions (qualitative and/or quantitatively) and has also allowed characteristic fingerprints to be established. This has helped in the understanding of local impact of emissions from sources such as floating roof tanks, local plant fugitives, emissions from loading activities and even emissions from effluent discharges (since volatiles in solution can evaporate to become an air quality issue). The program has benefited the site significantly in understanding local air quality issues and is becoming increasingly valuable as environmental legislation and regulation increases e.g. application to annual EALs (Environmental Assessment Levels) and demonstration of proactive environmental management.

An example of an air quality station for DMs (in-house design) is shown. This portable telescopic design uses stainless steel fittings mounted in a concrete base. It has a capped top and provides secure locations with some weather protection for up to about 16 DMs, as well as the capability to secure pumped sampling systems and other devices.

*(Design specifications are available on request).*

## Occupational Hygiene Applications

DMs have a huge practical advantage in occupational hygiene applications due to their inherent simplicity, reliability, small size and user acceptability. It must be emphasised though that they are not a replacement for personal observation. However, given that many occupational exposures are subject to multiple variables then DMs allow rapid collection of TWA (Time Weighted Average) data to assess log normally distributed exposure measurements against compliance with exposure limits.

Generally, DMs are seen as only capable of giving relatively long TWA data, although in some circumstances this can be reduced to smaller fractions of an hour due to excellent

detection sensitivities if thermal desorption is used as the analysis technique.



Photograph of a perimeter station and close-up of diffusive monitoring tubes positioned under the steel cap.

One novel use of DMs has been to extrapolate TWA data to give a potential "Exposure Equivalent Level" (EEL). The EEL concept, an idea taken from the noise term SEL (Sound Equivalent Level), has been employed at the BP Hull site in several recent exposure studies. This has greatly helped understand the potential impact of very short-term exposures by using DM derived results based on longer averaging periods. If an 8-hour TWA is considered and, providing task assessment shows this to be the case, is extrapolated to an equivalent dose over a shorter period of time then an

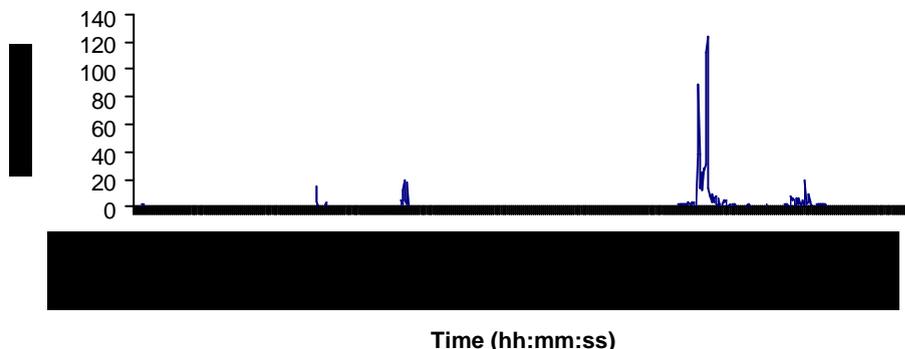
estimation of peaks in exposure can be calculated as shown in the example below.

Time Averaged Period	Example Concentration ppm	Comment
8 hours	1	Diffusive monitoring derived 8-hour TWA example concentration.
15 minute	32	Hypothetical derived 15-minute exposure equivalent level.
1 minute EEL	480	Hypothetical derived 1-minute exposure equivalent level.
1 second EEL	28800	Hypothetical derived 1-second exposure equivalent level.

Explanation of the EEL Concept Applied to DM Derived Results

This example shows how a DM derived 8 hour TWA can be used to calculate potential short-term dose equivalents. Some large numbers emerge from relatively low 8-hour TWA results. Professional judgment from the occupational hygienist must be needed in the application of this hypothetical concept. This approach has allowed a greater appreciation of peak exposures and how these can be masked when just considering long-term derived TWAs. Real time measurements used in conjunction with DMs can show variations from zero exposure to 2 orders of magnitude, or more, above the DM calculated TWA in real workplace exposure situations, especially where actual tasks are of short duration and close to point source emissions. Application of the EEL concept to DM derived TWAs therefore enables these peak exposures to be estimated – given task knowledge and observation. This concept has proved very successful in understanding issues associated with product loading activities, particularly where measurement techniques have been limited, for practical reasons, to DM based methods. An example of this from a recent study associated with jetty loading activities allowed full shift (8 hour TWAs) data to be used in estimating exposures over short-term tasks and potential peak exposures.

**Solvent Loading Activity**



Example of a solvent handling activity highlighting variability of exposure using a real-time exposure monitor (data-logging photo-ionisation detector).

## Report on Montpellier

*David L. Bartley, Richard H. Brown, Derrick Crump, Eddy Goelen, Theo L. Hafkensheid, Jan-Olov Levin, Robert G. Lewis, Ruud Peters, Hans-Ulrich Pfeffer, Kevin J. Saunders, Evelyn Wright and Emile De Saeger*

The International Conference 'Measuring Air Pollutants by Diffusive Sampling' was held in Montpellier, France from 26-28 September 2001. It was organised by the Institute for Environment and Sustainability of the European Commission's Joint Research Centre (Ispra, Italy) in collaboration with ADEME (France), Air Languedoc Roussillon (France) and Keris Ltd. (UK) with the support of a number of national and international organisations.

It was attended by approximately 275 participants from member states of the European Community, the so-called New Accession States, Norway, Switzerland, and – despite the unfavourable travel conditions – overseas countries (United States, South America).

Held fifteen years after the first Conference on Diffusive Sampling and ten years after the Clean Air at Work Symposium – both held in Luxembourg – this International Conference seemed long overdue. The seemingly long interval of 10 years, however, has made this conference one in which many novel aspects of diffusive sampling could be demonstrated.

Whilst in the 1986 and 1991 conferences, important focuses were on aspects such as the development of samplers and applications were found mainly in the domain of workplace air monitoring, the presentations in the 2001 conference have shown a transition both from development to application and from practical use for workplace air monitoring to – largely – ambient air monitoring.

From the various presentations, it has become clear that diffusive sampling has become a popular measurement methodology in application areas where emphasis is on ease of use, unobtrusiveness, low cost, measurement of time-integrated concentration levels and high spatial measurement density. The target pollutant, of course, needs to be a gas or vapour pollutant: particulates diffuse too slowly for this method to be of practical benefit with current technology. And although the shift from development to application suggests that diffusive sampling has matured as a measurement technique, the 2001 conference still revealed a lack in harmonisation of some aspects related to the practical applications of diffusive sampling. Particularly aspects of QA/QC, validation and assessment of measurement uncertainty deserve further attention.

A full report of the proceedings has been published by EC/JRC (report EUR 20242 EN) and a limited number of free copies are available on request from JRC's "European Reference Laboratory of Air Pollution" [erlap@jrc.it](mailto:erlap@jrc.it)

## **Monitoring Ambient Air – European perspective on Particulates and Photo-oxidants**

A meeting of the AAMG - Royal Society of Chemistry.

In co-operation with, Joint Research Centre, Ispra, Italy,  
National Physical Laboratory DTI VAM programme  
and the Health and Safety Executive.

**Wednesday 11<sup>th</sup> and Thursday 12<sup>th</sup> December 2002**  
**Scientific Societies Lecture Theatre, London**

Pollutants in rural and urban air include ozone, VOCs, PAHs, dioxins and micro particulate material. Concentration levels and distribution of these pollutants present an interesting challenge to analysts. Measurement methodologies require an understanding of the sample and sample matrix, careful design and development of methods to obtain robust procedures and quality data. However confidence levels are more variable and interpretation of results in context is often a challenge.

The aim of the conference is to create an opportunity to present to both the scientific community and public authorities recent developments in monitoring strategies, requirements and analytical techniques. Papers will be presented that cover the monitoring of pollutants and their effects on air quality in the rural and urban environment.

The conference will be of interest to industrial, public health and environmental chemists who are involved in air monitoring, environmental and health studies.

Further information may be obtained from:

### **Meeting and Registration Contact**

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Further details of this and other AAMG meetings can be found on the AAMG website at [www.aamg-rsc.org](http://www.aamg-rsc.org)

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