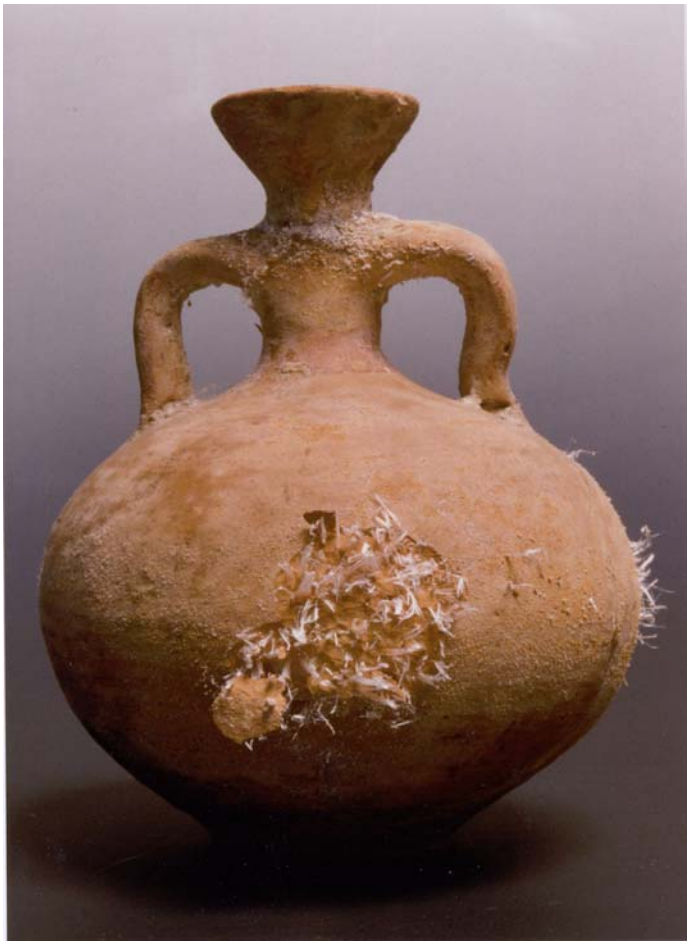

IAP Copenhagen 2001

4th meeting of the Indoor Air Pollution Working Group

Presentation Abstracts

The National Museum of Denmark
Conservation Department
November 8th-9th, 2001

NATIONALMUSEET

IAP Copenhagen 2001
4th meeting of the Indoor Air Pollution Working Group

Presentation Abstracts

The National Museum of Denmark
The Prince's Palace, Copenhagen, Denmark
November 8th-9th, 2001

Editor: Morten Ryhl-Svendsen

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All presentation abstracts in this publication can also be viewed online, some of them with additional illustrations compared to this document. The entry to all online IAP meeting abstract volumes (from 1998) can be found at: http://iaq.dk/iap.htm

Cover photo:
Calcium acetate chloride pentahydrate efflorescence on a terra cotta vase, probably caused by organic acid vapour from display case materials.
From the presentation of Lieve Halsberghe (page 25). Additional information about this particularly vase can be found on the Internet: *Efflorescence on a terra cotta vase, Cyprus, 650 B.C.*: http://iaq.dk/image/cyprus_vase.htm

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Foreword

The perception that preventive conservation is a key factor in preserving our cultural heritage has gained foothold in the Conservation Department of the National Museum of Denmark, as in most other cultural and historic institutions. What is achieved by performing complicated and costly conservation treatments on objects, if the objects are just returned to a silent but on-going destruction in a harmful environment?

The destructive actions of light, inappropriate temperatures and humidity are well recognised. However, in recent years we have become more and more aware of the unwanted, and often unexpected, effect of indoor air pollution on our collections. We have given this new area of research a high priority, and therefore are happy that the Indoor Air Pollution Working Group chose the National Museum of Denmark for their annual meeting in 2001. By providing such a framework for the meeting, it is our hope that the level of importance for this subject will increase, here and elsewhere.

Many interesting papers were given during the two-day meeting, and many important subjects were discussed. Almost of equal importance were the breaks between sessions where contacts were being made and visiting cards exchanged. One outcome of the meeting is that this volume of abstracts, together with last years, set yet another stone in the foundation of the Indoor Air Pollution Working Group as a serious party of the museum world's preventive conservation forum.

I thank the coordinators of the working group for an interesting and important meeting,

Jørgen Nordqvist
Director, Conservation Department
National Museum of Denmark

IAP Copenhagen 2001 - Conference Report

The 4th meeting of the Indoor Air Pollution Working Group (IAP Copenhagen 2001) was held on November 8-9, 2001. The meeting was organized by the Conservation Department of the National Museum of Denmark. The IAP group is an independent interest group focussing on air pollution and air quality problems in the museum environment (comprising museums, archives, libraries and historic buildings). Since the beginning of the group in 1998, meetings have been held annually.

The meeting was open to anyone sharing an interest in museum climate, and attracted about eighty participants. The agenda was divided into four sessions, each concentrating on one of the issues: Air Physics and Chemistry, Communication and IAQ Problems, Pollution Monitoring and Control, and Particulates in Museum Air. Twenty-one presentations were divided over the two days meeting. A number of presentations are briefly summarized below.

The meeting was opened by Dario Camuffo, who, in his talk 'Microclimate: a difficult variable in museums', summarized the problems of controlling museum microclimate, due to poor HVAC design, or even due to limited technology for measuring climate parameters. The ability of controlling the indoor climate is vital for, among other things, reducing the deposition rate of pollutants on surfaces to a minimum. Failing to do so, convective motions may develop, with the result of depositing suspended particles on the room walls and ceiling at high rate via aerodynamic deposition

Presentations within the 'Air Physics and Chemistry' session dealt with issues such as surface reactions of deposited nitrogen dioxide in museum environments and its generation of nitric acid (Peter Brimblecombe), and the tendencies of copper and lead to corrode in formic acid atmospheres (Jean Tétreault). Andrew Calver discussed the role of display case ventilation in the reduction of internally generated pollutants. He presented simple methods to measure display case air exchange rate, in which CO_2 or N_2O was used as tracer gas monitored by occupational health data loggers.

In the 'Communication and IAQ Problems' session, Janet Hughes reviewed a situation at the National Gallery of Australia, where there was great concern over the use of hydrogen peroxide as a sterilising agent for the air conditioning system, and its effect of this on the collection. This debate went public and resulted in a questioning in Senate, followed by an inquiry, which, among other issues raised questions to standards for air quality in museum buildings.

The presentations in the 'Pollution Monitoring and Control' session dealt with various sampling methods. Maarten van Bommel and Jens Glastrup each described the use of SPME-GC/MS for active, short-term sampling of carbonyl pollutants. Franco de Santis presented the use of passive samplers for NO_2, NOx, SO_2, HONO and O_3 in conjunction with the European 5th Framework Project 'Microclimate Indoor Monitoring in Cultural Heritage Preservation' (MIMIC). Also connected to the MIMIC project, Marianne Odlyha presented the development of a damage assessment dosimeter, based on piezoelectric quartz crystals coated with tempera paints.

The ‘Particulates in Museum Air’ session included a talk on a dust level and composition survey at the National Museum of Denmark (Anne Lisbeth Schmidt & Kåre Kemp), where dust levels were compared between an air conditioned gallery, a naturally ventilated gallery, and outside the museum (high rate of urban traffic). William Esposito, who unfortunately couldn’t be present, had his paper ‘Particle Profiles and Filtration Effciency in Museums’ read out. Esposito's paper presented a method to evaluate a HVAC filter packs effciency by its ability to filter out polystyrene microspheres. This was illustrated in a study of the HVAC filters in three New York City cultural institutions.

Participants represented a great number of nations, and within these many different cultural and educational institutions. Representatives from various other indoor climate working groups were also present. It was interesting for the participants to be updated with the current state-of-science in Japan, regarding museum climate and preventive conservation. A special thank goes to Chie Sano from the National Research Institute for Cultural Properties in Tokyo, who accepted to present a paper on this subject on very short notice.

Likewise, it was very informative to be presented with a report from a workshop at *CLIMA2000*, a conference held by ‘Representatives of European Heating and Ventilating Associations’ (REHVA) two months earlier in Italy. This was presented by Livio de Santoli, who organized that workshop. There are several working groups “out there” from different fields, but with related agendas about indoor air quality in museums or historic buildings. It will prove beneficial to attend each others' meetings and to strengthen contact between the groups. This way the overlap of specializations between groups can be avoided; it will also be rewarding to discuss problems from the viewpoint held by different groups.

The effect of such a meeting to the local conservation community should not be underestimated. More than half of the participants were from Scandinavia, and it is certain that the professional awareness in our region to museum indoor air pollution problems has received a boost. And while it was a great joy to meet many familiar faces, it was especially pleasing that so many new people showed a sincere interest in museum environment issues and joined the IAP meeting.

This meeting could only turn into reality because of the big support I received from the Conservation Department at the National Museum of Denmark. On behalf of the Indoor Air Pollution Working Group, I wish to thank director Jørgen Nordqvist, and head of laboratory Mads Chr. Christensen, for the wholehearted encouragement they gave me from the very first day when I presented to them the idea of hosting the IAP 2001 meeting in Denmark. Likewise, I would like to thank the Conservation Department for the financial support, which made the meeting possible.

Morten Ryhl-Svendsen
Conservation Department
National Museum of Denmark

Microclimate: A difficult variable in museums

Dario Camuffo, Giovanni Sturaro, Adriana Bernardi, Emanuela Pagan, and Francesca Becherini
National Research Council
Italy

Abstract

While the external climate has strongly influenced planning in the past, today modern technology creates the desired microclimate inside buildings with powerful systems to heating, ventilating, air conditioning (HVAC), and lighting. While in many cases highly satisfactory levels of comfort for people have been reached, the situation is rather more complex and problematical for the conservation of works of art. In some cases, the microclimate in museums is controlled for human welfare during opening times, and is left to evolve freely during the night. When the HVAC is switched on/off, the room environment undergoes abrupt changes, and also in the following it is continually perturbed by many factors. Field surveys show that the weak point of HVAC is not the production or absorption of heat or vapour, but rather the redistribution inside the rooms in order to obtain a climate which is homogeneous throughout the space and which is constant in time. Field surveys performed to do a sound environmental diagnostic in a number of European museums have found some weak point that are particularly common and that have been removed, or mitigated, after having been recognised. Some useful examples are as follows:

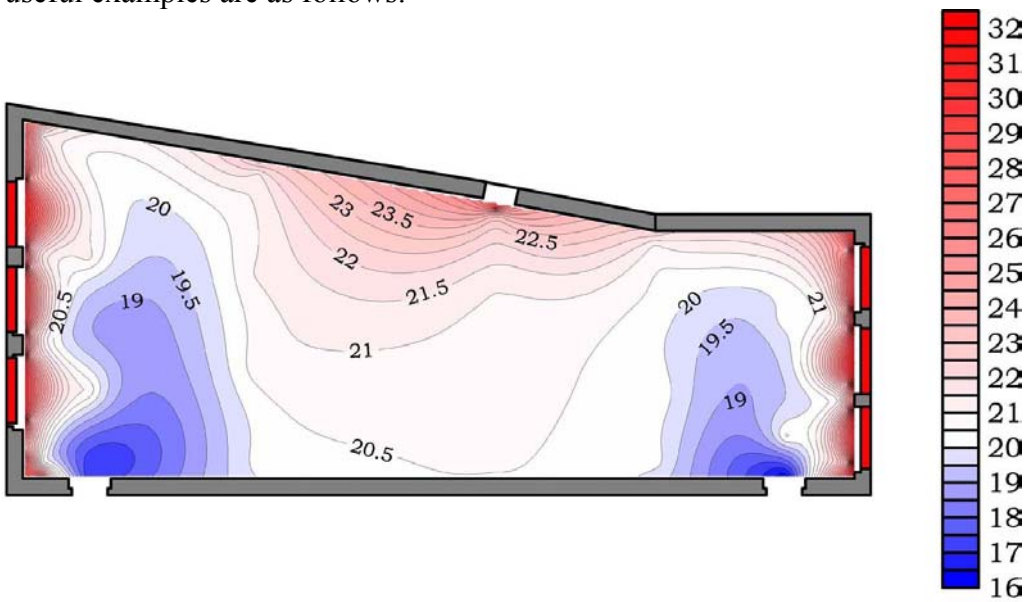


Figure 1: Floor temperature (ºC) with cold areas in front of two open doors determined by the entrance of air from the nearby cooler corridor. Room heating is made with radiators (red rectangles on the shorter sides) and floor heating. Hall of Giants, Padova (I), measurements taken in the occasion of a concert.

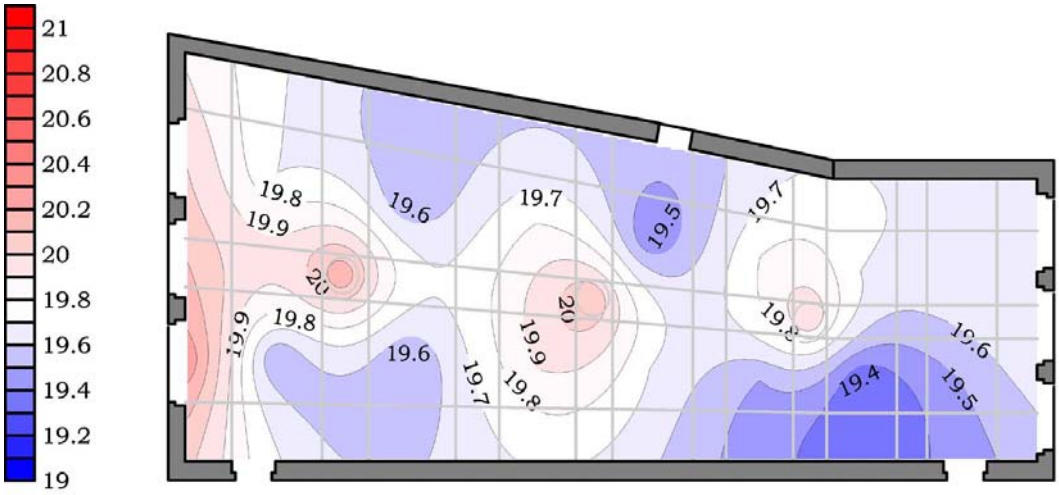


Figure 2: Wooden ceiling temperature (ºC) with hot spots determined by three chandeliers with 20 compact fluorescent lamps. Hall of Giants, Padova (I), measurements taken in the occasion of a concert.

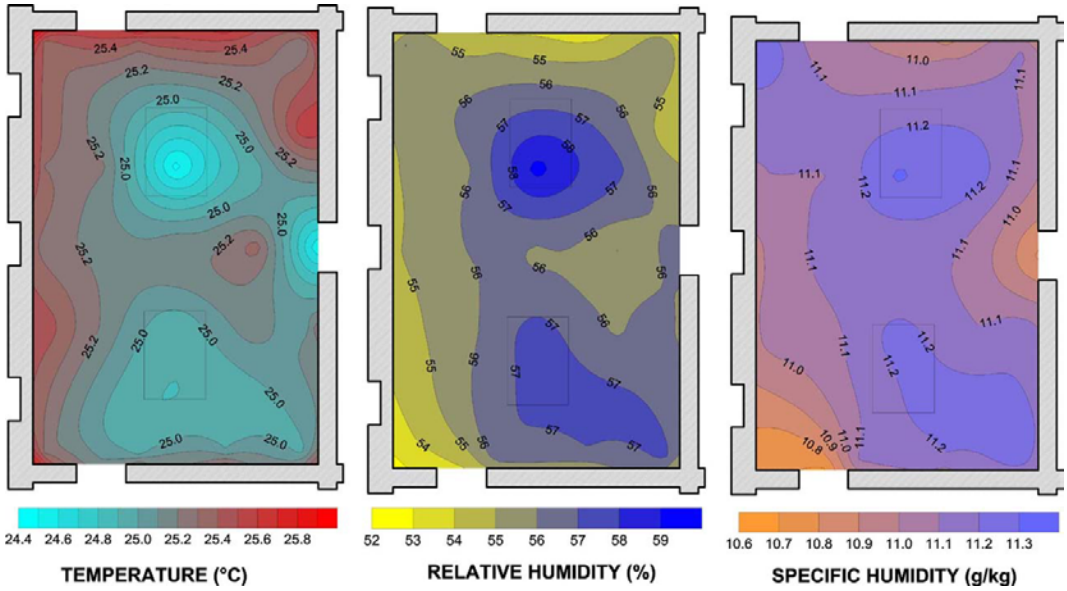


Figure 3: Effect of air conditioning with emission in the middle of the Bruegel Room, Kunsthistorisches Museum, Vienna (A). The air with different temperature and moisture content is appropriately released far from the paintings. The entrance of cooler air from the room on the right is also evident.

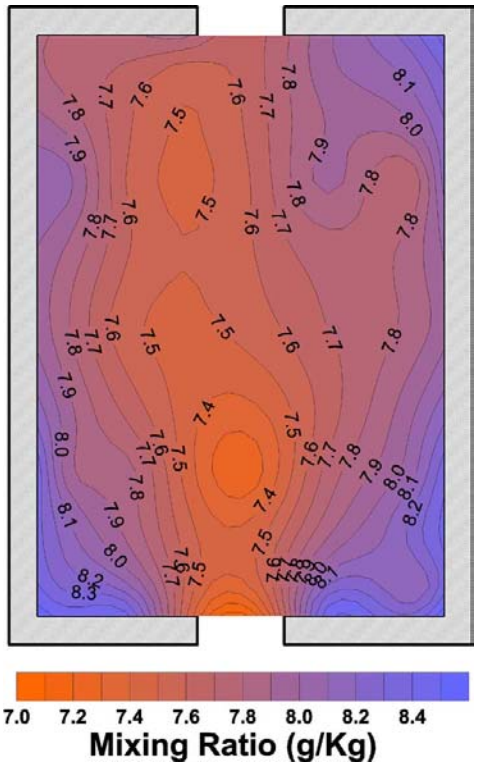


Figure 4:
Horizontal distribution of the mixing ratio inside a room in the Koninklijk Museum voor Schone Kunsten (KMSK), Antwerp (B). This parameter pinpoints the entrance of air from the door in the lower part of the drawing and shows how it spreads into the room.

The indoor microclimate conditions should be controlled also with the aim of reducing to a minimum the deposition rate of pollutants on surfaces. This requires that the air and the wall temperature are always at the same level, the floor is colder than the ambient air and the ceiling warmer. If things are different, convective motions develop, with the result of depositing suspended particles on the room walls and ceiling at high rate via aerodynamic deposition

Technology can not always resolve the various problems that arise, nor can it always reconcile mass tourism with conservation, which are hardly compatible each other. We cannot define a microclimate, or microclimate changes, absolutely safe for conservation in general terms, but we should look at the impact it causes on the individual artworks, especially the most delicate ones. A problem is that we can detect the most evident and immediate damages, not what will happens in the long term as a result of the cumulative effect of many cycles. An agreement about the thresholds of the allowed microclimate perturbation is still lacking, and we need more laboratory tests and field surveys to better relate environmental causes, artworks response and damage assessment.

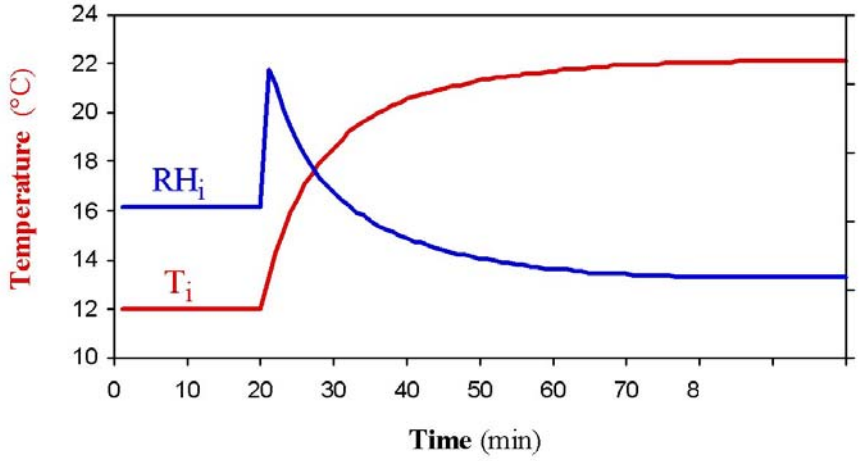
The study of the microclimate for the conservation of works of art presents various difficulties. First among them is the fact that appropriate measuring instruments are not always available since, basically, only instruments designed for other uses are commercially available. The study of interactions between works of art and the environment requires knowledge of the physical parameters which characterise the object and the corresponding atmospheric values. Rarely can the same instrument be used to measure both the object and the environment. Valid instrumentation is often unavailable to measure objects of art while satisfying both requirements of precision and absolute respect for the work of art, which on its own would require only no-contact measurements.

It is not easy to measure the temperature of an art work which cannot be handled following a style well established for industrial or meteorological purposes. Contact measurements are always difficult because of the incomplete adhesion of the probe to the surface of the artwork that may be rough or uneven. In the industrial field adhesives are sold to improve thermal contact, but their use on artworks is inappropriate when they stain the surface. In case of paintings on canvas or isolated sheets of paper, the thermal capacity of the sensor is much greater than that of the artistic work, so that in this case it is the thermometer which imposes its temperature on the object, and not vice versa. Whenever possible, for non-metallic works of art, or for highly oxidised metallic objects, it is preferable to take thermal measurements based on the infrared emissions of the object. In this case the sensor should be placed inside a golden metallic cup, so that it is shielded from the radiation of the external environment and it will collect all the direct and reflected radiation emitted from its surface. Under these conditions, measurements are independent of the specific emissivity of the surface and may reach values of high precision, if the electric circuit compensates for the thermal drift of the instrument. Unfortunately, most of the instruments in the market are not adequately compensated for to reach a high accuracy.

To further complicate matters, the characteristics reported in the technical sheets of commercial instruments are sometimes ambiguous. In some cases the factory declares the characteristics of the sensors, without specifying how these are transformed by the presence of the casing and the whole chain connected to the measurement. The most common consequence is a major increase in the time response with significant repercussions on temperature measurements and, above all, on humidity.

For example, Fig. 5 gives the results of a commercial hygrometer with nominal response-time of the order of 1 minute, placed in a climatic chamber, the square wave cycles going from 0 to 100% of relative humidity (RH) in a 45 min period. The sensor is very quick, but, once placed in its plastic support, it undergoes such inertia that in every cycle, it reaches only 40%. If some of the plastic is removed from the less essential parts of the casing, measurements reach 60%; if all the plastic is removed leaving the sensor practically isolated, but next to the supply line and control panel, 70% is reached. If the instrument is calibrated in the laboratory and left long enough, it becomes precise. The problem is that the declared response-time only reflects the characteristics of the isolated sensor and not the whole instrument, which is unsuitable for dynamic field measurements as it provides unreliable data.

Figure 5:



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Surface reactions of deposited NO_2 in the museum environment

Peter Brimblecombe, Michele Raychaudhuri, and Derek Bowden
University of East Anglia
United Kingdom

Abstract

EFFECTS OF NITROGEN DIOXIDE
Traditionally this gas has been associated with the degradation of dyes, fabrics and other organic materials, although some recent work has argued in favour of its adjunct, nitric acid playing a greater role in damaging items indoors.

INDOOR CHEMISTRY of NO_2
Nitrogen dioxide chemistry involve three potential processes in indoor air.
1. Production of nitric acid
2. Rapid equilibration with ozone and nitric oxide (NO)
3. Surface chemistry indoors where it generates nitrous acid (HONO)

1. NITRIC ACID PRODUCTION
This is the product of oxidation
$NO_2 + OH \rightarrow HNO_3$
$NO_2 + O_3 \rightarrow NO_3 + O_2$
$NO_3 + RH \rightarrow R + HNO_3$
Normally NO_3 is a night time process in the outdoor air, but indoors much lower light intensities allow it to be active.

2. INDOOR OZONE CHEMISTRY
INDOOR/OUTDOOR NO_2 ratios change in the summer to become higher. This is thought to be due to reactions with indoor ozone in large buildings with high air change rates and low absorbace surfaces
$NO_2 + O_3 \rightarrow NO_2 + O_2$

3. NITROUS ACID EMISSIONS
$HONO + hv \rightarrow OH + NO$
$OH + RH \rightarrow R. + H_2O$
$O_2 + R. + M \rightarrow ROO. + M$
$ROO + NO \rightarrow RO + NO_2$

REACTIONS AT THE SURFACE
Probably fast:
$H_2O + 2NO_2$ (ads) → HNO_3(ads) + HONO(ads)
In alkaline conditions the HNO_3, and HONO will convert to the anions: NO_3 and NO_2 .
What happens to NO_2?

NITRITE REACTIONS
Initially we have investigated the behaviour of nitrite (NO_2) in materials
1. constructional materials
2. ageing plaster
3. breeze-block
4. concrete tile
5. wool
NO_2 was present in fresh plaster and doesn't oxidise or get lost...
Some penetration from external air into Breeze blocks, but little change at depth..., suggesting that some NO_2 was inherent in the material.
Little evidence that NO_2 deposited on wool is released over time or of nitrite oxidation.
However nitrite present in wool appeared to increase over time.
Especially at elevated temperatures, possibly as a result of degradation of protein or release of bound nitrite?

DEPOSITION VELOCITY [Vd]
Fundamental parameter to describe indoor removal rate and describing absorption of NO_2 from air...
NO_2 DEPOSITION VELOCITY
Measurements of NO_2 onto concrete floor tiles show a strong RH dependence reminding us of the important role of water...

HYPOTHESES ABOUT NITRITE
Ubiquitous in porous non-acidic materials
Originates in situ and via deposition
Long lived and strongly bound (unexpected)...?
Threat to conservation needs modification... textiles and HNO_3
Re-emission as HONO may not predominate in total flux terms

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Copper and lead corrosion in carbonyl environments

Jean Tétreault[1], Emilio Cano[2], Maarten van Bommel[3], and David Scott[4]
Canadian Conservation Institute [1]
Centro Nacional de Investigaciones Metalúrgicas (CENIM), Spain [2]
Netherlands Institute for Cultural Heritage (ICN) [3]
Getty Conservation Institute, USA [4]

Abstract

For the last 12 years, there has been an increasing interest on indoor air quality in museums and archives. Sensitive monitoring techniques have been developing for carbonyls and a better information are available on the typical off-gassing of construction products. However, some object - pollutant interactions were not yet fully investigated. Many data refer to the effect of acetic acids to metals but formic acid was less covered in conditions which interest museums and archives.

The aim of this project is to gain a better understanding of the tendency of copper and lead to corrode into a few months period in rich carbonyl environments frequently observed in display or storage settings. The research has two parts:

1) determination of the non observable adverse effect level (NOAEL) of formic acid for copper and lead at 54 and 75% RH at 21ºC
2) determination the effect of presence of many different carbonyls on the corrosion rate and on the NOAEL.

Humid carbonyl environments are generated by carbonyl water salt mixtures in glass jars. Metal coupons were suspended above the mixtures for 135 days. The corrosion of metals will be investigated by weight gain measurement, colour measurement and XRD with low angles. Based on the XRD results, the mechanism of corrosion by carbonyls and strategies for controlling the damage to copper and lead in enclosure can be suggested.

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Measurement of case exchange rates and the use of such measurements

Hubertus Ankersmit*, Maximiliano Lebidinsky, and Simon F. Watts
Oxford Brookes University, United Kingdom
Instituut Collectie Nederland / Netherlands Institute for Cultural Heritage (ICN) *

Abstract

The results of some case exchange experiments is reported. The case used for these experiments had a volume of 1.5 m^3 and composed of 4mm polycarbonate sheets with pre-drilled holes covered with duck tape (see slides from presentation).

N_2O, temperature, and relative humidity were measured at various points inside and outside the case. The N2O was squirted into the case (maximum total concentration was 5%) and the concentrations of N_2O, RH and temperature measured with time. This set-up was chosen as it gives the basis of a simple and economic method for the measurement and interpretation of case exchange rates in working (*i.e.* with artefacts) museum cases.

Data from the laboratory case was presented and showed a number of characteristics:

1. The decay of the levels of RH and N_2O were broadly consistent.
2. The data showed a very interesting second order dependance (i.e. 1/[N_2O] vs time) was a straight line
3. The determined exchange rate varied not only with the cross section of the holes, but also as a function of the position of the holes

Some of this behaviour was attributed to the particular design of the test case, and in particular the second order variation of N_2O - this behaviour has not been observed in other comparable cases and is thought to be the effect of the dissolution in the adhesive of the duck tape as it leaves the case.

Following four pages: Presentation slides

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IAQ 2001

Observations from a Museum Case

Simon Watts, Max Libedinsky and Hubertus Ankersmit*

School of Biological and Molecular Sciences, Oxford Brookes University

*The Netherlands Institute for Cultural Heritage

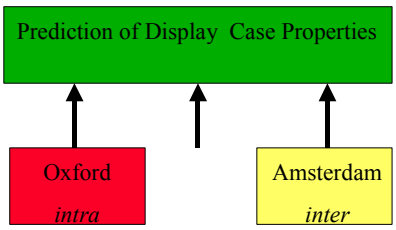
OXFORD BROOKES UNIVERSITY

Aims of this work

- To study *intra*-case differences of some chemical and physical parameters
- To identify appropriate parameters for case function description
- To test the Michalski type model for exchange processes

Inter-relationship with other work

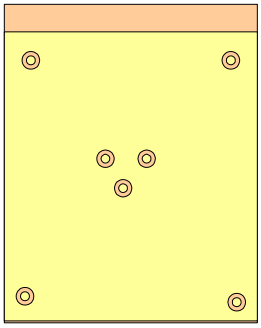
- Frank Ligterink, Maarten van Bommel & Hubertus Ankersmit (Institute for Cultural Heritage, Amsterdam)
- Andrew Calver (Museum of London)



The "Case"

- Dimensions 1m x 1m x 1.5 m
- Steel with plastic fixing and 4mm polycarbonate sides
- Corners with silicon sealant

"Case" Specifications



- Holes
  - 1 cm diameter
- Cracks (along top)
  - 0.7 and 2.5 cm width
- Sealed with "Duck" tape

"Case" Layout

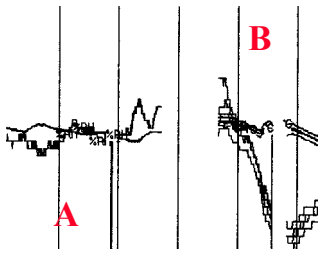
- Monitoring the "Case"
  - Meaco Museum Control System
    - R_H, T at 3 points in case
      - top front LHS corner
      - centre
      - bottom RHS corner
      - outside bottom LHS corner
  - Analox N_2O "Buddy"
    - N_2O, T at 1 point in case
      - mid front
- N_2O inlet middle LHS and computer fan bottom LHS front corner

The working "Case" I

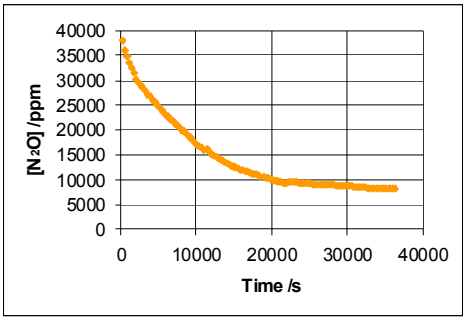
- The experiments involve injecting N_2O into the case and watching the loss under varying conditions

The "Case" Geography

- Differences in temperature between four probes
  - (A) ~ 0.5ºC
  - (B) ~ 3 ºC
- Tells us that inside the case is not well mixed (hotter at top)

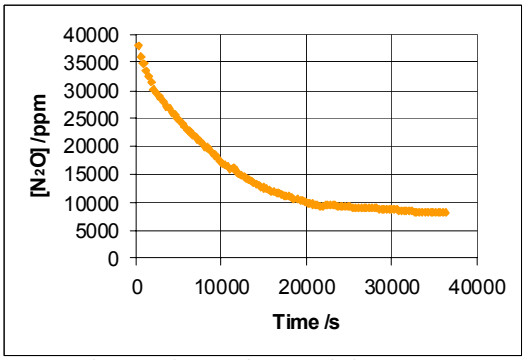


The working "Case" II



- Decay curve from fully closed case
- Slope (rate of exchange) gets progressively less
- Need a model or mathematical description before analysis & comparison

Interpretation

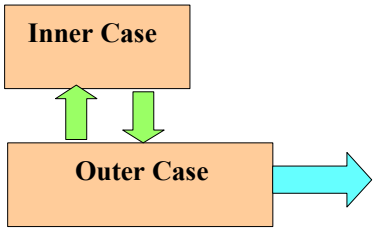


- The "Why" of a model
- Not a good fit to any of the expected models - NOT continuous curve
- Approximate N_2O lifetime in case ~ 27 hours (CER 0.89 d^{-1})

The working model I

- Observations
  - Temperature differences mean stratification inside case - such stability implies separate air-masses
  - Would explain "kinks" in curves and areas of decreasing slope
- Guessed two reservoirs - two stage box-model [Truesdale, V.W. Watts, S.F. [2001] Deep Sea Research **

The working model II

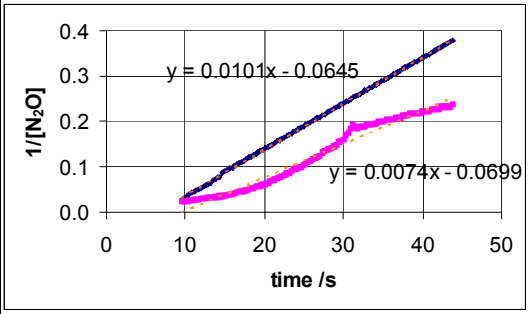


$$\frac{1}{a}\ln\frac{(a[N_2O]_t - b)}{[N_2O]_0} = t$$

- *a* & *b* are constants, *t* is time, and $[N_2O]$ is N_2O concentration

First Test

- Use of fan should make case atmosphere uniform, shorter lifetimes, higher CER.
- Fan should fit standard model, this graph second order (!)
- Mauve without fan, black with fan. Steeper line, higher CER



Implications

- Fan increases CER by ~ 30%
- Fan straightens out kinks, better fit to standard models (second order not understood!)
- Normal museum cases do not have fans - hence CERs better than predicted - Michalski's model does not comprehend second box

Affect on CER of holes

- Tests limited
  - holes at same level
  - holes at different level
  - no cracks (yet!)

Cross-sectional hole area / 10^6 m^2			Height Difference / m	Slope of 1/[N2O] vs t line / 10^6 ppm^{-1}
Fixed*	Variable (planned holes)	Total (Fixed + Variable)		
300	78.60	378	0	0.004
300	157.1	457	1.40	0.008
300	157.1	457	0	0.007
300	314.2	614.2	1.40	0.010

* (CER 0.88 d^{-1}; Case volume 1.5 m^3;P_s = 0.25 Pa.)

Conclusions

- From this work (in progress)
  - *intra* - case effects are important for medium sized cases
  - Michalski model does not seem to deal with inhomogeneous air masses within cases very well
  - More work is required to validate the entrainment type model

Non-spherical holes and wavy tracer gas decay curves. A comparison of theory and real life with respect to leakage of display cases

Frank Ligterink, Hubertus Ankersmit, and Maarten van Bommel
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Abstract

Conservators and curators from time to time will have to decide on the design of new display cases or the implementation of measures to improve existing display cases. Sometimes cases have to be well sealed in order to prevent penetration of harmful components from the external environment. In other situations a certain level of ventilation is preferred in order to avoid the accumulation of harmful components emitted either by objects or construction materials the interior of the case.

To guide the design of cases, at least a crude quantitative estimate of the effects of various measures that influence the leakage/ventilation rate of a case is necessary. In principle the equations and graphs in Stefan Michalski's article 'Leakage prediction for buildings, cases, bags and bottles' [1] allow for such estimations.

In his article Stefan Michalski distinguishes three basic transport mechanisms, which determine the leakage of display cases:

1) air flow through holes and cracks
2) diffusion through (stagnant air in) holes and cracks
3) permeation through case wall materials

The airflow through holes and cracks is driven by pressure differences across the holes. Equations are given for pressure differences caused by air density differences between inside and outside due to temperature and relative humidity differences (stack pressure), and pressure differences caused by thermal and barometric pumping. The equations developed in the article are based on the assumption of homogeneous conditions within the case. Stack pressure is considered constant. Flow and diffusion equations through the holes and cracks are developed for simplified geometry's, that is tube shaped holes and rectangular cracks.

In real life, display cases seldom have simplified geometries and temperature and relative humidity differences are not constant. It is tempting to create more precise models that can account for this level of detail . From a practical (non-physicist) point of view, however, the current set of equations is already complicated to work with. In this study the practical use and the validity of the leakage predictions made by Michalski are tested experimentally. Exchange rates of a display case with holes and cracks of different sizes, shapes and positions are measured using carbondioxide as a

tracer gas, while internal and external temperatures, relative humidities and air speed are measured simultaneously. The decay in the carbondioxide concentration allows for calculation of the actual exchange rate, which is compared with values calculated with the theoretical ones. Aim of this work is to produce a ready-to-use set of equations that can be implemented in a spreadsheet program to predict exchange rates of display cases.

Reference:

[1] Michalski S., "Leakage prediction for buildings, cases, bags and bottles", Studies in Conservation, 39 (1994) 169-186.

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The ventilation of enclosures to reduce internally generated pollutants and simple techniques to measure air exchange rates within enclosures: Report on progress to date

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Abstract

The presentation will outline the work undertaken to date for the research programme outlined below. The key work so far has been to develop equipment for simplified tracer gas measurement of the air exchange rate of display cases and other enclosures following on from the work briefly shown at IAQ2000 [1]. This information can be used to measure ventilation rates for passive ventilation systems or conversely to determine the air tightness of the case. The equipment used in the experiments is readily available, compact, battery powered and can be used within existing enclosures. The start up cost for the equipment and numerous tests is approximately the same for a single commercial test making the measurement of air exchange rates a viable additional tool for investigations into air quality and enclosures. Results to date from the study of the internal levels of key carbonyl and sulphur compounds measured on the same ventilated and non-ventilated enclosures will also be presented. It is hoped that this will stimulate discussion of the merits the pros and cons of ventilating enclosures for different types of materials, different display or storage conditions and climates.

Summary of current research programme:
Since the Museum of London opened in 1976 it has had a policy of ventilated display cases wherever practicable - that is to deliberately enhance the air exchange rate using filtered ventilation ports. This approach is contrary to the current trend for very low air exchange rate cases. This approach originally appears to have been to circulation the air to prevent the build up of dust and stagnant or damp air but more recently the aim has been to reduce the concentration of internally generated pollutants. In this case the primary aim was to reduce the concentration of potentially damaging organic compounds emitted by display case construction materials, however, more recently concern has focused on the potential for the objects themselves to out gas undesirable compounds. The Museum of London is a social history museum with a wide range of materials and object types from archaeological and historical contexts. Pollution studies have shown several archaeological objects from waterlogged sites produce gaseous sulphur compounds, which have proven to promote the tarnishing of silver objects housed in the same case. The primary method of providing ventilation has involved variously sized vents located at the top and bottom of the case. The vents are fitted with

particle filters to reduce dust ingress and the airflow through the case is assumed to be driven by stack pressure. Some previous pollution monitoring results have suggested that the cases without ventilation have higher pollution concentrations however no visible ill effects have been observed on objects in these cases.

With the move by other museums towards very well sealed display cases with air exchange rates of less than 0.1 air changes per day and the adoption of this specification by many case manufacturers it was felt that the museums strategy should be reviewed. The addition of vents can add considerably to the cost of a case and benefits of reduced air exchange such as humidity buffering and the reduction of externally generated pollutants may also be lost. However, experience has shown that the ventilation adds a measure of protection against the build up of high relative humidity levels caused by condensation within cases against cold external walls - a common problem in the Museum of London as the building is humidified to 50% in the winter and insulation levels are poor. Proposals for major gallery redevelopment's meant that in order to justify the need or otherwise for ventilated display cases further research would be required. In theory air movement through the vents in the case will dilute the concentration of internally generated pollutants leading to lower equilibrium concentrations. There is increasing empirical and experimental evidence to suggest the damage caused by carbonyl compounds such as acetic acid on susceptible may only occur above certain concentrations. If this is the case then control by dilution could be a simple and effective mitigation technique that can be retrofitted to many types of traditional case and storage enclosure.

To determine the effect in real situations pollution monitoring studies will be carried out in existing display cases and storage enclosures especially where previous monitoring data exists. Levels of acetic acid, formic acid, acetaldehyde, formaldehyde, hydrogen sulphide and carbonyl sulphide will be measured internally and externally using diffusion tubes in the enclosures normal ventilated mode and then again after the vents have been sealed to reduce as far as possible the air exchange rate. One of the key factors governing the internal concentration is likely to be the ventilation or air exchange rate of the enclosure as this governs the dilution factor and influences the emission rate. Although it assumed that the ventilated cases do in fact ventilate the enclosure more than a similar unventilated case no measurements have ever been undertaken at the Museum of London to check this. Therefore not clear what effect, if any, the various types and designs of vents have had. Indeed in almost all reported cases of pollution levels measured in cases and enclosures the air exchange rate has not been reported. While a variety of methods have been used in the past to measure the air exchange rate of cases the most readily available method is tracer gas decay. This is an effective technique, which is commercially available in the UK and relatively simple if you already possess a suitable portable gas analyser. Unfortunately if you do not possess the equipment the current method is prohibitively expensive for routine measurements and requires external equipment and thus sampling ports in the case making it difficult to use on existing cases or enclosures without such a facility.

The initial challenge was to find a cost effective method to measure air exchange rate in cases that could ideally be used in both existing cases containing objects in the galleries. Previously reported simple attempts to measure air exchange rate have used changes in relative humidity (using water as a tracer gas) or pressurisation measurements but both of these techniques have limitations. As the tracer gas technique is effective and relatively simple the first approach has been to investigate the availability of smaller and cheaper gas sensors. An inexpensive carbon dioxide sensor connected to a radio telemetry monitoring system was on trial at the museum for measuring carbon dioxide levels in galleries (as a measure of air quality). This led to an examination of using CO_2 as a tracer gas rather than the nitrous oxide (N_2O) used commercially. Initial results showed promise. However, as CO_2 is an atmospheric gas and bioeffluent the background concentration varies depending on occupancy. Following some initial studies a relatively inexpensive data logging N_2O sensor was obtained and tested alongside the CO_2 sensor. Initial results are promising with good repeatability and the methods will be tested alongside the commercially available method in an attempt to test their accuracy. Simple methods of tracer gas delivery have also been explored using domestic supplies of CO_2 (for inflating cycle tires) and N_2O ('whippets' for aerosol cream) to avoid the need for bulky and expensive cylinders and regulators.

Reference:
[1] Andrew Calver: Conservation, "Research and the Budget – A Real World View", IAQ2000 Oxford-Brookes, http://iaq.dk/iap/iaq2000/2000_18.htm

Next page:
Slides from presentation: N_2O monitor, whipped cream gas delivery mechanism, air exchange rate measurement set-up.

The full presentation (55 slides, approximately 1.5 MB files) can be viewed on the Internet: http://iaq.dk/iap/iap2001/2001_06.htm

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Medigas PM 3010

Handheld infra-red N_2O monitor

Environmental Instruments

- Small self contained logger
- Rechargable NiMH battery (750 Ah = 8hrs pump off, 6hrs on)
- Integral pump with tube attachment
- Range 0-1000 ppm 0-10,000 ppm for leak detection
- Accuracy at constant temperature
  0-100 ppm +/- 10 ppm
  500-100 10% of reading
  temperature effect 2.5ppm/ºC offset
- cost £1000, 11600 Kr.

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Enclosure air exchange kit Mk2

- whipped cream gas delivery mechanism

- fan with 30 minute clockwork switch

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Mark 3 - extended battery life

7Ah sealed lead acid battery

c. 72 hrs battery life

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The conservation of ceramics contaminated with acid induced salts: Necessity of a multi-disiplinary approach

Lieve Halsberghe
Independent Belgian ceramics conservator,
living in Luxemburg

Abstract

When conservators are confronted with ceramics contaminated with salts, it is practically impossible for them to identify the salt contaminants present. And yet it is essential information to determine the kind of treatment and still more important to determine what will be the best environmental conditions for its later conservation.

Acid induced salts are even more complicated and many contain phases that are still unidentified. Their growth can be rather slow, but their action most destructive since most have hydrated forms. Moreover, the acid acts throughout the body of the ceramic and decomposes the calcite present. (*Editors note: see photo on front cover of this volume*)

Desalination is no longer believed to be the best treatment for salt contaminated ceramics. But on the other hand, there are not yet enough data available on the properties of these salts and their behaviour in complex mixtures of salts, to be able to determine the ideal relative humidity.
Several scientists are studying the properties of these salts, but they often lack the confrontation with the salts on the objects themselves. Conservators are eager to learn more about the problem to be able to choose the best treatment for the conservation of the object on a long-term basis. Curators will want to know what are the best preventive measures to be taken, at a reasonable cost.
For the sake of our heritage, it is absolutely necessary to work together and exchange our thoughts and experiences.

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Clearing the air: communicating air quality issues to museum staff and responding to external accusations at the National Gallery of Australia

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National Gallery of Australia

A recent journal article mused that one day in the future, the current Director of the National Gallery of Australia, an Irishman, will look back on his time in Australia and recall one of the idiosyncrasies of the Australian arts scene, and will surely reply: "You have to understand Australians are passionate about their air-conditioning". Indeed this would be a reasonable prediction based on the numerous questions asked in Parliament and countless media articles written on the recent air conditioning problems of the NGA building (Ford 2000). Australians could be expected to be passionate about air conditioning in the variable climate of the national capital, Canberra, which is cold (often below -5ºC) in winter and often over +35ºC in summer. Air conditioning is vital for visitor comfort and to protect the collections - but what happens when a former conservator alleges that HVAC operations and maintenance were putting the collections at risk.

This paper describes briefly the methodology and conclusions of the investigation of indoor air pollution (IAP) issues at NGA and discusses the difficulties of communicating the risks to collections in the absence of comprehensive, agreed, evidence-based standards.

There were two classes of allegations concerning the NGA HVAC:
1) Health/safety, and 2) threats to collections.
The health allegations were wide-ranging including poor standards of hygiene, inadequate training, improper handling of chemicals and lack of response to reported building problems.
This paper focuses on the threats to collections. The NGA collections cover a wide range of materials including works on paper, paintings on canvas and panels using various media, textiles modern and ancient from around the world, glass, metals and a large collection of Aboriginal and Torres Strait Islander art of diverse materials including bark, wood, feathers, leather, and other plant materials.

The consequences of the allegations have been 18 months of adverse TV, radio reports with many articles in the press, including some on the front page of national newspapers. Senior NGA staff were called to answer detailed questions at Senate Estimates hearings in the Australian Parliament and there were two statutory investigations by the Australian Government Occupational Health and Safety agency (Comcare), as well as an enquiry by the Commonwealth Ombudsman.

This situation caused considerable staff anxiety and disruption because of the time required to address the allegations.
In the preparing this paper we formed the impression that this media and Parliamentary interest in IAP issues in museums was unusual. This experience highlighted the problems of investigating and communicating these issues when, at the time of the investigation, there were no agreed IAP standards giving specific guidance for museums.

Gallery air risk to treasures

SUSAN McCULLOCH-UEHLIN
❑ Visual arts writer

THE nation's premier art collection could suffer irreversible damage from the National Gallery's air-conditioning system, a former head conservator warned yesterday.

Former National Gallery of Australia head conservator Bruce Ford has written to gallery director Brian Kennedy and Arts Minister Richard Alston outlining his concerns.

He says they are based on a report issued in April by the government agency Comcare and a recent Senate estimates hearing in which the NGA director and senior staff were questioned about the findings.

"I understand the NGA's building services has been using hydrogen peroxide ... to clean organic material from the air handling units ... leaving a residue of hydrogen peroxide in the tanks," he wrote. "The (air conditioning) ducts are kept clean by the same mechanism."

If hydrogen peroxide was active in the ducting system, it was highly likely it would reach storage and display areas, Mr Ford said.

"As a strong oxidising agent, hydrogen peroxide is an extremely destructive chemical ... it depolymerises (breaks down) many natural and artificial fibres such as wood, cotton, bark, wool, some plastics and most organic dye stuff."

This would affect thousands of the gallery's works.

"Think of the Asian textiles, the Aboriginal bark collection, works on paper and many of the decorative arts, just to mention some," he told *The Australian*.

Mr Ford has received an acknowledgment from Dr Kennedy, who said he would "look into the matter".

With an honours degree in chemistry, Mr Ford was conservation scientist at the NGA from 1989 to 1992 before becoming head of conservation in 1992.

The Comcare report was instigated earlier this year following complaints by an "anonymous informant" relating to health and safety.

Dr Kennedy said yesterday he was "preparing responses" to questions from the estimates committee.

First word The dollar Weather

Figure 1: This is but one example of the media coverage in national newspapers

The serious nature of the allegations necessitated an independent enquiry. Following discussions with the Institution of Engineers, Steve Hennessy, a mechanical engineer, was selected to conduct the enquiry to produce a comprehensive report for the NGA Director.

The enquiry commenced in June 2000 and proceeded over several months due to complex microbiological testing requirements and additional information produced during the investigation. At the initial investigation meeting with NGA staff it was apparent that health allegations could readily be dealt with by reference to comprehensive, detailed standards (*e.g.* risk-based standards for Legionella). This could not be done for allegations regarding the collections, particularly concerning the H_2O_2 concentrations. The investigation could not be extended for the years that would be necessary to develop such standards! NGA Conservators supported the investigation to determine whether some problems observed during collection surveys were due to HVAC or other causes.

The history of development of IAP standards is well known to this audience but a brief review is given here to provide some context of the approach to the NGA issues.

Thomson provides longstanding standards on NOx, SO_2, ozone and particulates. More recent investigations have focussed attention on the impact of carbonyl pollutants on enclosed spaces, and it is excellent to have this information collated on a website thanks to Morten Ryhl-Svendsen.

Tétreault provides an excellent overview of the types of standards that should be considered:

1) Acceptable risk concentration
2) Background level (cf with external concentrations)
3) Dosage (concentration x time)- but problematic where deterioration is not linear with time
4) No-Observed Adverse Effect Level (NOAEL)- requires knowledge of concentration, temperature, RH, time, property measured
5) Threshold level (reaction kinetics and thermodynamics)

Padfield provides thought-provoking comment in several papers and letters (in references) on perils of reliance on numbers at the risk of understanding the effects.

Cassar *et al* compared IAP in HVAC and non-HVAC buildings in London concluding that HVAC did not significantly improve control of IAP except for NOx and particulates.

The NGA case study examines role of HVAC in controlling IAP in a 'clean' city.

Building commenced in 1978 and it was opened in 1982. It is typical of many large modern art galleries of the period built extensively of concrete. Lower levels have art storage, workshops, loading dock. There are two levels of galleries and top floor contains administration area including Conservation lab. The building has a history of problems including roof membrane leakage, condensation especially in winter, dust from bush-hammered concrete. These problems have been progressively fixed over the past few years, but this has been expensive.
NGA frequently attracts media attention, being located in the maligned national capital unloved by the competing major cities of Sydney and Melbourne.

The HVAC system is quite complex due to needs for RH control. Being an inland city with prevailing low RH means dehumidifiers are not standard equipment, but humidifiers of varying types have been used throughout the building's history. Of the nine AHUs in the original part of the building, four have spray humidifiers and one AHU has a steam humidifier. Filtration varies according to the type of space, being highest for spaces with works of art.

A new 1,600 m^2 extension gallery has nine additional AHUs, each with its own chillers, filters and steam humidifiers to enable close control of conditions for blockbuster exhibitions. HVAC costs are considerable. A major building refurbishment and enhancement project costing USD 21 million over 3 yrs will include extensive work on the HVAC system.

The crucial issues arising from the allegations are whether H_2O_2 aerosols are carried from the humidifiers via the ducts to areas where works of art are displayed or stored. H_2O_2 is used monthly to clean microbial growths from the humidifiers, particularly the cooling coils, as these can be expected to grow in continuously wet conditions. A biocide is used to kill the organisms and H_2O_2 breaks up the organic matter. A 50% solution is diluted to 1%v/v in the trough and circulated through the sprayers for two hours, then drained and cleaned off with pressure sprayers. The fans are turned off. There are no museum standards available for max. permitted concentration of H_2O_2 so the approach was to measure air movement and concentrations throughout the dosing and cleaning process. Air movement was found to be insignificant using standardised sensor measurements. Peroxide concentrations were measured in air and water samples from two AHUs subject to detailed testing. Test methods were colourimetric (for water) and Draeger® tubes used calibrated measurements of reaction with potassium iodide. Despite this extensive testing, those making the allegations have not been satisfied and it remains difficult to refute the allegations absolutely without evidence-based standards although it is also unrealistic to expect these could be developed without several years of research.

Figure 2: Cleaning of the humidifiers

Fig. 2 shows the pressure spraying underway to rinse off peroxide used in the monthly cleaning of the humidifiers. Note the sprayers at left and troughs at lower left, where the peroxide solution is poured in and diluted for circulation.
Note: without the use of peroxide the cleaning process would not be as efficient in killing microorganisms in the humidifiers, *i.e.* the peroxide supplements the use of biocides. Without such cleaning there could be an enhanced risk to public health, so there is an issue of balancing concern about the use of any chemicals (especially an oxidising agent) against the assurance of public safety.

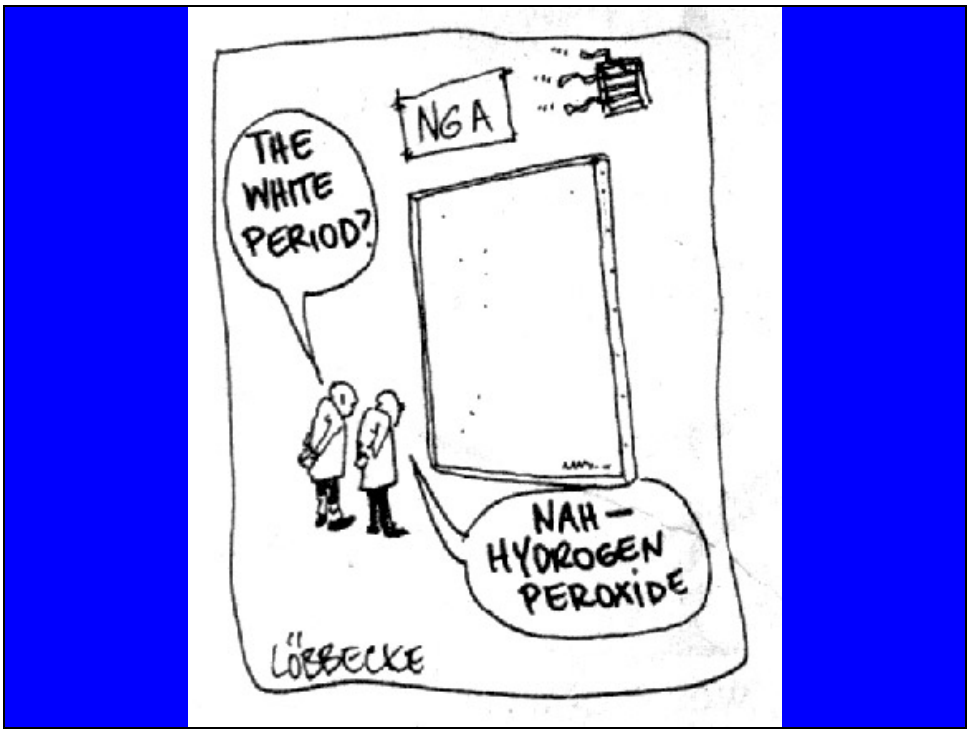

Figure 3: A lighter moment during the investigation (from Ford 2000).

Broad scale surveys of collections are done regularly at NGA and three significant problems were identified over recent years where the cause could possibly be due to IAP.

1) Fatty acid blooms on some 100 paintings could be due to the known previous problems with alkaline particulates due to the use of bush-hammered concrete walls, but instances have arisen in other paintings by the same artists due to pigment-binder interactions.
2) Weeping glass on some 10% of the collection stored in the building could also be due to alkaline particulates distributed by HVAC, but could also be due to unstable composition or other causes.
3) Silver tarnishing was another known long term problem in the Small Object Store with approx 2/3 of the silver items in this area affected. This could be due to air quality from HVAC or from the cabinets.

A central issue of the investigation is whether agreed risk factors are actually causing the observed problems. Apart from the H_2O_2 tests, particulate measurements were made throughout the building using Grimm particle analyser.
In addition a series of alkalinity, fatty acid and greasy film tests were used to determine whether this is the cause of the fatty acid blooms in the painting store. A 'grab sampling' method using a sealed vacuum canister with absorbents was used to collect gaseous pollutants for GC-MS analysis.
Various water samples from humidifiers were analysed, particularly 'dissolved sulphide' and 'easily released sulphide' to determine whether the HVAC is a source affecting the silver collection.
(Results are available from the authors and a paper discussing the methodology and results has been submitted for ICOM CC Rio 2002)

Figure 4: Sampling in the silver cabinet in the Small Object Store. Note the wood and plywood construction of the cabinets, which are over 20 years old and were lacquered with Paraloid B72. The silver items are placed on archival paper.

There is a need to balance health requirements to effectively clean the humidifiers against the very low risk that H_2O_2 might cause damage below the detection limit. Nevertheless, the high labour costs of this cleaning method are such that alternative humidification methods have been sought: an atomising system has been successfully installed in one AHU and ultrasonic methods are being considered which are easier to maintain and offer energy savings.

Gaseous pollutants complied with the existing standards except in three samples from the Paintings Store, Silver Cabinet and in one gallery. Alkalinity and fatty acid results showed that alkaline particulates were not the source of the fatty acid blooms.
Failure of pressurisation control was a concern on the lower floor that is believed responsible for the high results for SO_2 and greasy films. This is being addressed in ongoing upgrading of the HVAC system and further tests will identify if this has been successful. Any changes in 'gas scrubbing' efficiency will also be monitored as the old spray and steam humidifiers are replaced by ultrasonic ones.

The NGA HVAC system is a significant operating expense, one of many that must be considered by the Director in managing the budget. To communicate the priorities for achieving good control of IAP in museums it is necessary to be able to relate conditions in one's own institution with some form of accepted standards. Without these standards or accepted best practice guidelines it is difficult to defend one's position when challenged.

For chemicals known to cause significant damage to collections, conservators require some form of evidence-based standard, either NOAEL, although working towards threshold data would be useful. Where unusual chemicals are questioned, such as hydrogen peroxide, then perhaps comparison with background levels or some acceptable magnitude lower than OH&S standards may be the only option given that research resources required to establish standards are unlikely to ever be available.
A further concern is whether the low IAP levels required to prevent damage to collections are achievable/affordable. This drives the 'acceptable risk' approach to standards and may be suitable as an interim measure if the consequences of the risk can be defined.
Acceptance of a best practice methodology and guidelines such as those of the Museums Association in UK would make it easier to present a case for resources to address IAP issues in museums, especially since this guide also specifically addresses energy efficiency.

The investigation refuted the allegations that the HVAC system was causing damage to collections. The NGA case study provides some analytical data suggesting practical bounds for IAP in a modern air conditioned building in a 'clean' city.
The investigation focussed attention on IAP issues at a high level - suggesting both standards for maximum concentration and guidelines for approaching the problems are required to provide some measure of authority for comparing the performance of individual institutions against some form of 'best practice'.
Guides to best practice, even allowing for lack of established IAP standards will help conservators to communicate priorities for dealing with IAP issues in museums.

The full presentation (19 slides, approximately 0.5 MB files) can be viewed on the Internet: http://iaq.dk/iap/iap2001/2001_08.htm

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Indoor environment engineering for heritage conservation: Report from a workshop at the *Clima2000* conference

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Abstract

The conservation of cultural heritage needs expertise in Indoor Environment Engineering (IEE) to assist conservators and curators in monitoring and conditioning the indoor environment to minimise the damaging effects by poor environmental conditions. The conservation of works of art requires clean air and suitable and stable environmental conditions. The main aim of the workshop in *Clima2000*-Napoli 2001 was to discuss and identify the needs for further development in research, practice and manufacturing and to establish a REHVA Working Group to carry out guidelines for Indoor Environment Engineering for cultural heritage conservation, in connection with existing ISIAQ WG21 "IAQ and climate in cultural and heritage collections".

The main aims of the Workshop have been the following:

- to define the role that experts in air conditioning can play in cultural heritage conservation
- to discuss the needs for further research and development in the field of IAQ and HVAC
- to establish a REHVA Working Group (in connection with existing ISIAQ WG21 "IAQ and climate in cultural and heritage collections") to carry out guidelines for indoor environment engineering in cultural heritage conservation.

trying to provide answers to the following questions, representing different sections of a tentative Guidelines:

- Hygro-thermal Environment
- Air Quality
- HVAC systems and components
- Showcase's microclimate

Links:

REHVA web site: http://www.rehva.org

IAQ and climate in cultural and heritage collections:
http://www.ie.dtu.dk/isiaq/TaskForces.asp?TF=3

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Does monitoring in a museum help to improve environmental conditions? *- or -* The Monitoring at the Germanic National Museum, Nürnberg, and its consequences

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Abstract

1. Monitoring
In 1999 the Germanic National Museum started two investigations:

1. *A general survey on monitoring*
   asking about 70 German museums with an answering rate of 60%
2. *A 'Monitoring case study'*
   in the Nürnberg Museum looking at critical points in the collection and depots

1.1 The survey
The general survey revealed a chaos concerning all areas of monitoring:

1. There is no contact to specialized laboratories
2. No museum ever did a general monitoring on its location to learn systematically about its conditions
3. In nearly no German museum the conservators have the authority to intervene in matters of monitoring, they simply rely on continuous arguing or persuasion
4. The conservators knowledge of detecting systems is very low
5. Detecting is usually done by scientists
6. but all museums claim to be aware museums of their environmental problems and observe fast aging surfaces.

1.2 The 'Monitoring case study'
The actual impetus to put forward a monitoring was a high amount of dust and greasy layers on show cases and objects. Dirt is something the top management in a museum dislikes, since dirty show cases and objects render neglecting the care for the collection.

The peaks of result:
The dust in the ventilation pipes had plaster, soot and rubber. But as well:

- Lead (2.200 mg/kg)
- Copper (520 mg/kg)
- Zinc (9.900 mg/kg)
- Cadmium (54 mg/kg)

In the show cases we detected:

- Acetic acid: 140 nng/m3 - 54 = 5,6 ppm
- Formaldehyde: 64 nng/m3 - 41 = 5,33 ppm, the German standards allow 0.3 ppm

The air in one show room was polluted by:
PCB (700 mg/kg), The German standards allow 1 mg/kg

2. The semi - profession of the conservators

The results of the monitoring study case had its impact. The conservators were faced with the argument: If you want us to change the products, you have to name them.

Although having introduced tests on relevant materials in a newly opened dependance on armoury the controlling passive sampling months later detected all those VOCs, we like to be absent.

3. Monitoring is not only detecting gases

If we understand monitoring only as scientific measuring, there will be no changes in our museums. Monitoring as well means looking for appropriate material.

In reaction of our experiences we started to test any material in our laboratory.
Since then we have about 50 tests. By the time we will have the problem to find the tests in our folder for further use. So a databank must be developed.

But testing materials revealed clearly another problem: Monitoring delays planning. So far, in the timetable of museum planning monitoring does not appear.

4. Monitoring as reaction on problems -Monitoring as a program

Actually conservators always react on demands rather than act on developing the issue. We work without a system and there is no manpower even to scope with every day demands. Non systematic work is waste of time and money.

Therefore teams must be installed to handle problems of monitoring in both ways, the every day demands and the systematic work on material and monitoring. Presently this can only be done with a project. In cooperation with the Bavarian National Museum, München, a concept had been developed. We formulated the following two essentials:

1. Conservators must be equipped with a certain amount of detecting facilities they can use independently. It must be easy to handle, cheap and reliable. This detecting set does not to dispense with scientific analyses. Independent and reliable detecting at low costs must be the first step.
2. There must be established a list of materials appropriate in a museum. It is clear, this list has to be rewritten constantly, since the brands change constantly and many incrediants are not to be declared.

5. Conclusion for the future

In the long run there must be established a new profession in the museums:
The engineer for museum environment.

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The fight against indoor air pollution

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Abstract

The deleterious effects of indoor air pollutants, such as acetic acid, formic acid and formaldehyde, on museum artefacts have been recognised for many years. A project was set up which dealt with a number of aspects of this problem. The project involved the construction and validation of an atmospheric sampling chamber, the development of a novel sampling method for the detection of pollutants and the reduction of pollutant concentration using mesoporous scavengers. Also, in an attempt to understand the synergistic effects of carbonyl pollutant concentration and humidity on a range of materials, the project will assess the damage caused by different polluted environments on a variety of materials commonly found in museums.

Validation of atmospheric chamber
A series of chambers have been constructed in the University to permit atmospheric testing of enclosed polluted environments. The polluted environments are generated by flowing air over heated permeation tubes. The permeation rate of the tube, and thus eventual pollutant concentration, is controlled by selection of the desired oven temperature and gas flow rate. Thus, a wide range of accurate pollutant concentrations can be studied. The pollutants selected for inclusion in this study are formaldehyde, acetic acid and formic acid. Validation of the pollutant concentration generated inside the chamber is critical. In order to confirm the gas concentration inside the chamber, the pollutants are measured using passive sampling methods of analyses. Validation experiments for acetic acid, formic acid or formaldehyde contaminated environments will be performed over the range 100 ppb to 5 ppm.

Once the testing phase of the exposure system has been completed, environments containing mixed pollutant vapours will be generated and used to determine the effect of interferent gaseous molecules on the current sampling methods used. In addition, active sampling methods will be developed to permit rapid detection of pollutant vapours.

Novel sampling method
One of the main aims of the project is to investigate the potential of novel non-invasive sampling methods for use in a museum environment. The first method to be assessed involves the preparation of a sol-gel (a glass support) and impregnation of the sol-gel with a specific chemical. The choice of chemical depends on the target pollutant, but in any case, it is intended to react with the gaseous target molecule after it diffuses into the porous glass support. In the first study, the ability of formaldehyde to react with a hydrazine-impregnated sol-gel will be assessed. If successful the sol-gel will be coated

onto an optical fibre and the colour change observed after reaction between the gas and the impregnated sol-gel using UV or Raman spectroscopy.

Mesoporous materials

At present activated charcoal is often used to remove deleterious pollutants from contaminated museum enclosures. It is thought that mesoporous silicates offer a number of advantageous over the sorbents currently used. These substances have a larger pore size than zeolites, typically 2 to 50 nm, allowing them to physically scavenge pollutants more easily. In addition, at present, the sorbents are normally tested in active mode, but it is thought that mesoporous substances could also be used effectively in passive mode. With their larger pore size it is also possible to chemically modify them, e.g. make them basic, thus increasing their selectivity for acidic molecules. One advantage of a chemically modified scavenger would be the elimination of back-diffusion problems currently encountered with activated charcoal. Mesoporous silicates have been prepared and are currently being studied using XRD to determine their structure. Porosity testing and surface analysis will also be carried out to determine the nature of the substances prepared. The mesoporous silicates will then be tested both passively and actively using the atmospheric chambers.

Effects of long term exposure on artefacts

A number of materials commonly found in the museum environment (e.g. limestone, eggshells, copper, bronze and lead coupons) will be subjected to different polluted environments for approximately 2 ½ years. Mixtures of formaldehyde, formic and/or acetic acid solution will be placed in sealed desiccators to provide a number of contaminated environments. All pollutants will be measured at approximately 1ppm and at either 40 or 100% RH. Experimental design has been used to define the experiments needed in order to obtain the most information from the study. The polluted atmospheres will be monitored regularly and the pollutants replenished when necessary. Material damage, which occurs as a result of exposure to the polluted environment, will be monitored by recording weight gain measurements over time. In addition optical microscopy and scanning electron microscopy will be used to study the surface of the materials. If necessary, XRD and chromatographic techniques will be used to identify corrosion products.

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Development of a damage assessment dosimeter using piezoelectric quartz crystals coated with egg based films

Marianne Odlyha, Gary M. Foster*, and Jonathan M Slater
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School of Engineering & Computer Science, University of Exeter *
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Abstract

In past years coated piezoelectric quartz crystals have been developed for selective and sensitive determination of air pollutants which include ammonia and hydrogen sulphide [1]. More recently polyethylene imine coated piezoelectric quartz crystals have been used for continuous monitoring of the relative humidity gradients across a painting in Sandham Memorial Chapel [2]. Gaseous materials can be selectively adsorbed by the coating causing a decrease in the frequency of vibration of the crystal and a measure of the gas adsorbed. Gases can also cause irreversible changes in the film and may provide a measure of the potential for damage of a particular indoor environment. In this paper the potential of egg based and varnish coated piezoelectric quartz crystals is discussed.

References:
[1] L.M.Webber,J.Hlavay and G.G.Guilbault, "Piezoelectric Detectors for Specific Detection of Environmental Pollutants", Mikrochimica Acta, 1 (1978) 351-358

[2] M. Odlyha, G. M. Foster, N. S. Cohen, C. Sitwell and L. Bullock, "Microclimate monitoring of indoor environments using piezoelectric quartz crystal humidity sensors", J. Environ. Monit., 2 (2000) 127-131

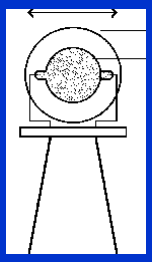
Next pages:
Slides from presentation: MIMIC project objectives, System used in MIMIC project, Coated PQCs for damage assessment, Coating of PQCs with tempera paint.

The full presentation (33 slides, approximately 1 MB files) can be viewed on the Internet: http://iaq.dk/iap/iap2001/2001_13.htm

Objectives MIMIC project

- Assess *damage* from integrated response of synergistic action of environmental factors (fluctuations in RH,T, levels of light and pollutants) using *array of PQCs*.
- Obtain early warning and indications of *risk* to objects through unfavourable microclimates.
- Possibility of using various coatings selective in their response to some of these factors (from data obtained in ERA project)

System used in MIMIC project



Quartz wafer

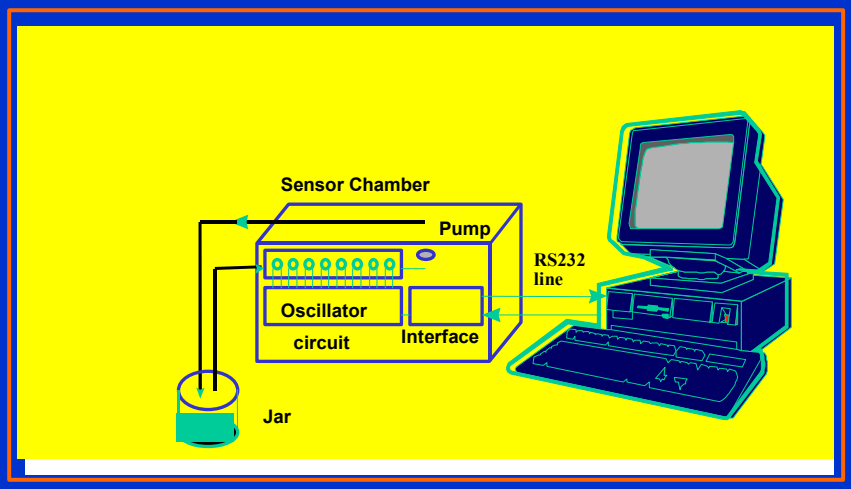
Gold electrodes on both surfaces

Connection pins

Coated PQCs for Damage Assessment

QuartzTec,UK

M.Appleton



Coating of PQCs

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The protection of cultural heritage and the use of diffusive sampling

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CNR - Istituto Inquinamento Atmosferico, Italy [1]
Anadolu University, Environmental Engineering Department, Turkey [2]

Abstract

The Protection of Artworks and Cultural Heritage is a first priority issue in Italy due to the exceptional wealth and substantial unique artistic heritage.
It is known that an approach based on a single point measurement without investigating local and temporal variations can give only partial information. A more comprehensive assessment should include a generalisation that covers the territory or, in a museum the study of more than one room. This can be made on the basis of the knowledge of the spatial distribution of concentrations in a specific area where an artwork is located. In contrast to active samplers in which air is brought into contact with a detector or collector device by means of a pump, diffusive samplers rely on diffusion to bring the pollutant into contact with the collector. Compared with the pump-dependent active sampling procedure (*i.e.* diffusion denuders), main advantages of the method are cost effectiveness, simplicity and the potential for large-scale measurements carried out at the same time. Passive samplers are an ideal tool for determining the pollutant distribution over a large area and 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. In addition, the passive device is not constrained to sites where electrical power is available.

A simple, inexpensive passive sampler for many pollutants has been developed. The sampler is a modification of the open-tube design obtained by using a filter treated with appropriate reagents to trap the pollutant. The device developed in this study is similar to that described by Bertoni *et al* [1] in previous laboratory and field studies of atmospheric benzene, toluene and xylenes (ANALYST®). The body of the sampler is a cylindrical glass vial with a threaded cap at one end. The pollutant is collected on a disc of impregnated microfibre or carbon paper filter 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 was protected using a fine stainless steel screen. Before and after sampling the screen is replaced with a polyethylene cap.

The typical questions an assessment by using passive sampling can answer are:

- find locations where a risk of excessive pollution exists and where certain conditions such as the compliance of thresholds is satisfied (spatial identification)
- find the differences within an area over time (trends). Primary interest arising from this research for conservationists is to determine the causes for deterioration and current status of the historic buildings and monuments in order to develop an appropriate treatment and conservation.

Examples taken from monitoring campaigns in the framework of the European Project MIMIC for NO_2, NOx, SO_2, HONO and O_3 at the Uffizi Gallery, at the Alcazar of Segovia, at the National Museum of Denmark, at the Sandham Chapel (UK) and for NO_2 and SO_2 in Siracusa, (Italy) will be presented and discussed.

Reference:

[1] Bertoni G, Tappa R, Allegrini I, (2000) Annali di Chimica 90:249-263

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Emission of organic acids from wooden construction materials in a small test chamber; preliminary results of optimisation of the Solid Phase Micro Extraction technique

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Instituut Collectie Nederland / Netherlands Institute for Cultural Heritage (ICN)

Abstract

Wooden construction materials, used in storage and exhibitions, are known sources for low molecular organic volatiles. The amount of organic volatiles depends, among others, on the type of wood. Especially particleboard and other composits such as MDF, are known to emit formic acid, acetic acid and formaldehyde, but other types of wood emit these organic compounds as well. In the last decades, much effort has been put in determining the effects of these emissions on objects of culture and art, e.g. by the well-known “Oddy test”. Furthermore, methods to reduce emission have been investigated. Appropriate lacquers, absorption materials or sealing the wood with impermeable films can reduce the emission significantly.

The damage to objects depends on the concentration of harmful gasses, the sensitivity of the material of the object, exposure time and environmental conditions. In the case of organic acid vapours and formaldehyde, the wooden construction material of the showcase is often the emitting source. The concentration organic volatiles does not only depend on the emission rate of the construction material, but also on the ventilation of the showcase. A high air exchange rate will in principle lower the concentration organic vapour, assuming that the outside air does not contain organic vapour. However, the exchange rate does also affect the emission rate of the construction material; a higher exchange rate will increase the emission.

At the ICN, research is focussed on predicting the final concentration of organic vapours in a showcase, in order to provide guidelines for the use of construction materials and the need of mitigation methods. For this, it is necessary to determine the emission rates of materials at different exchange rates. Usually, construction materials are placed into a small test chamber with the possibility to control the air exchange rate by flushing the test chamber with a variable airflow. The concentration organic vapours in the air is determined using various sampling and analysis techniques, however, none of these techniques is satisfactory in terms of sensitivity and speed. Lately, a new sampling technique, Solid Phase Micro Extraction (SPME), is introduced as a fast and sensitive method.

This presentation focuses on the sampling technique itself, in particular on establishing the relationship between the uptake by the SPME fibre and the flow rate of the air. Using a calibration gas, two different sampling techniques were compared: static and dynamic sampling. Static sampling is performed by flushing a glass jar with the calibration gas. Next, the glass jar is closed and the SPME fibre is introduced through a septum and exposed to the stagnant air. The advantage of this technique is that the sampling rate of the SPME fibre is independent of the airflow. Dynamic sampling is performed by sampling directly in the gas stream through an in-line injection valve. This presentation discusses the application of different SPME fibres, the effect of the airflow rate during SPME sampling on the amount of organic vapour collected, evaluation of the different sampling techniques and the calibration of the sampling technique used.

Next pages: Slides from presentation:

1) SPME fibre. The use of Solid Phase Micro Extraction for analysis: Compounds of interest absorb on the SPME fibre. Next the fibre is transferred to the injection port of Gas Chromatography-mass Spectrometry (GC-MS) and the compounds are desorbed due to the high temperature and analysed. See Supelco catalogue for more information (http://www.sigma-aldrich.com)

2) Climate chamber setup: A small test chamber is used for measuring the construction material.

3) Sampling method: static

4) Sampling method: dynamic

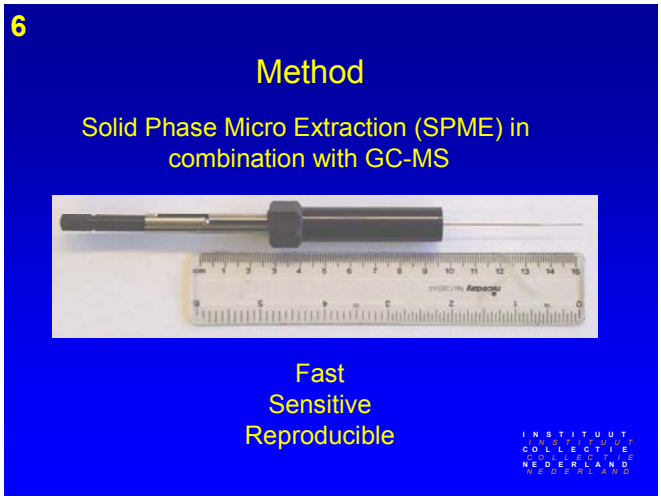
5) Several SPME fibres were tested:

PDMS / DVB polydimethylsiloxane / divinylbenzener
CAR / PDMS Carboxen / polydimethylsiloxane
CW / DVB Carbowax / divinylbenzene
DVB / CAR / PDMS divinylbenzene / carboxen / polydimethylsiloxane

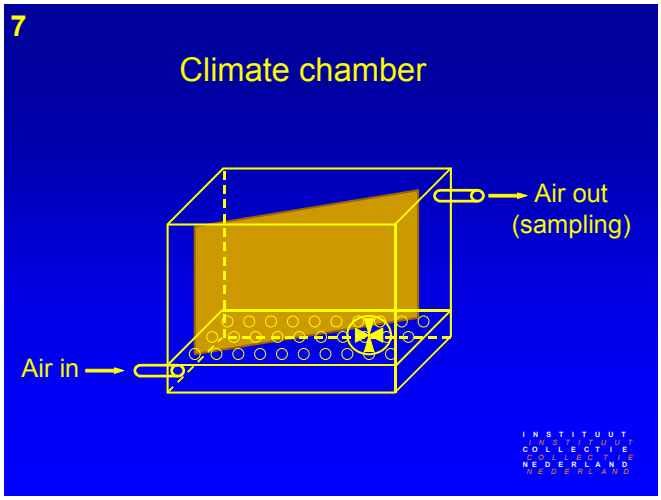
Detection limits of all fibres when they are in equilibrium with the exception of the Carboxen / polydimethylsiloxane fibre where the sampling time is reduced to 30 min.

6) Calibration curves of formic acid and acetic acid with the Carboxen / polydimethylsiloxane fibre after 30 min. sampling.

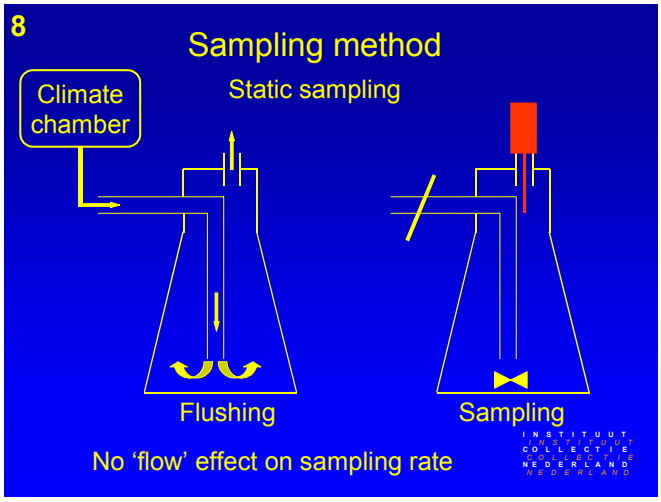
The full presentation (20 slides, approximately 0.8 MB files) can be viewed on the Internet: http://iaq.dk/iap/iap2001/2001_15.htm


6
Method
Solid Phase Micro Extraction (SPME) in combination with GC-MS
Fast
Sensitive
Reproducible
INSTITUUT COLLECTIEF NEDERLAND

1

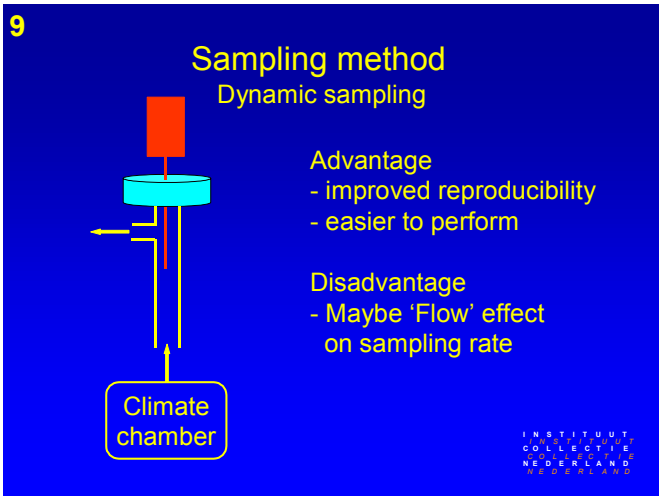

7
Climate chamber
Air out (sampling)
Air in
INSTITUUT COLLECTIEF NEDERLAND

2

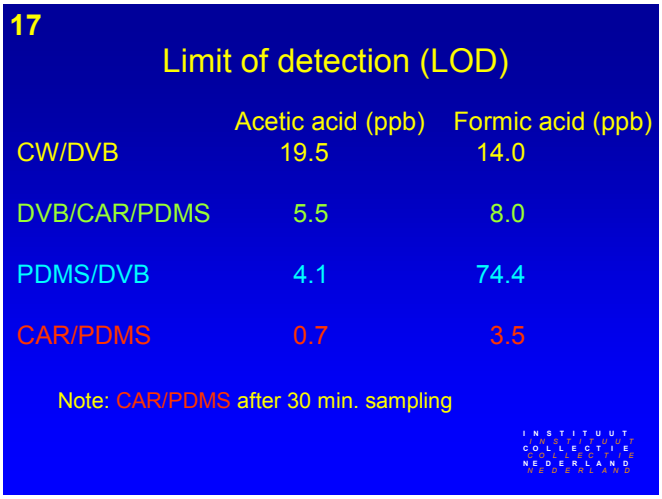

8
Sampling method
Static sampling
Climate chamber
Flushing
Sampling
No 'flow' effect on sampling rate
INSTITUUT COLLECTIEF NEDERLAND

3

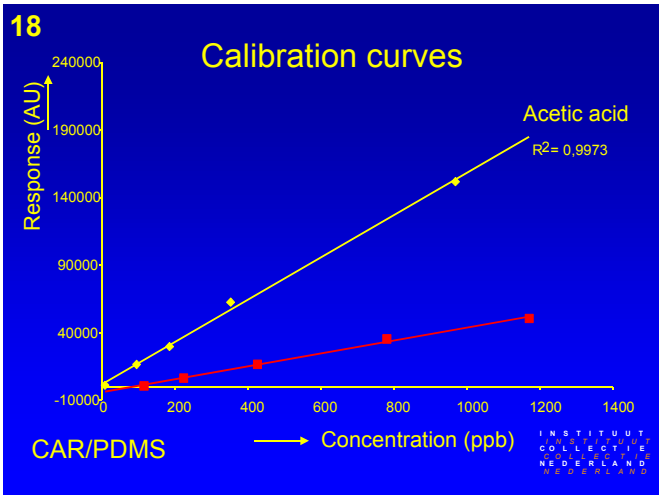
4


9
Sampling method
Dynamic sampling
Advantage
- improved reproducibility
- easier to perform
Disadvantage
- Maybe 'Flow' effect
on sampling rate
Climate chamber

5


17
Limit of detection (LOD)
Acetic acid (ppb)
Formic acid (ppb)
CW/DVB 19.5 14.0
DVB/CAR/PDMS 5.5 8.0
PDMS/DVB 4.1 74.4
CAR/PDMS 0.7 3.5
Note: CAR/PDMS after 30 min. sampling

6


18
Calibration curves
Response (AU)
240000
190000
140000
90000
40000
-10000
0
200
400
600
800
1000
1200
1400
Acetic acid
R2= 0,9973
CAR/PDMS
Concentration (ppb)

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Recent improvements in SPME-GC/MS detection of acetic and formic acid in air

Jens Glastrup and Morten Ryhl-Svendsen
The National Museum of Denmark

Abstract

1): Formic acid sampling:

Following what we presented last year in Oxford, about detection of acetic acid in air by SPME-GC/MS, we have now investigated the performance of SPME as a sampling media for formic acid also. The method and experimental setup are identical to the description in last years Oxford paper [1].

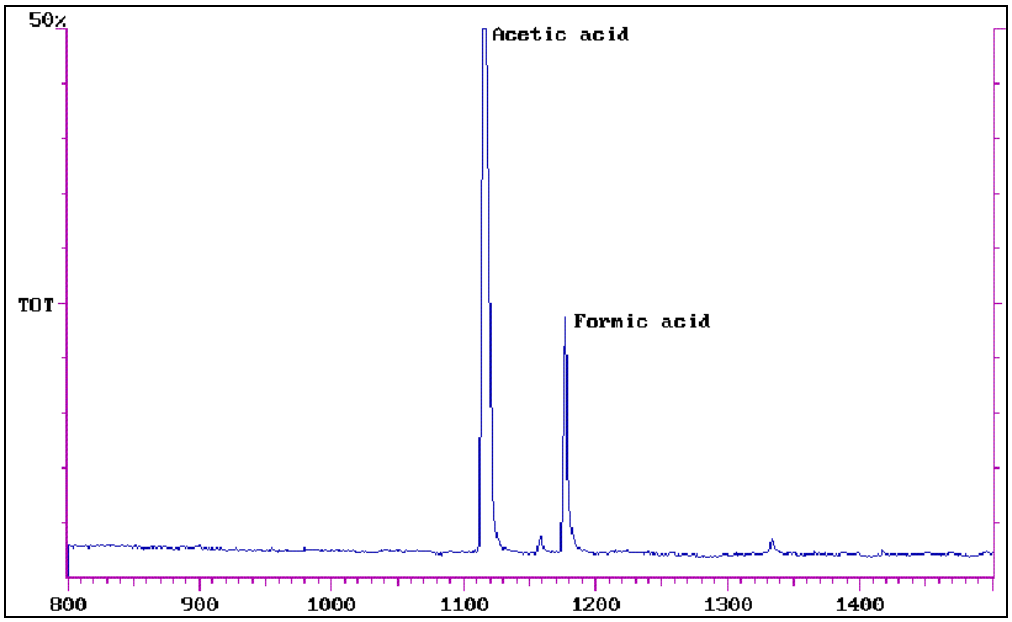

Figure 1: Chromatogram of acetic and formic acid in air, sampled on SPME (PA 85µ)

By exposing the SPME fibre (PA 85µm) to formic acid standards in the concentrations 10, 110, 210, 310, 410, and 510 µg/m3 (in triplicates), we have found a linear response between the standard concentrations and the GC signal with a correlation coefficient better than r=0.98. The detection limit of the method was 28.9 µg/m3.

By the same method we have previously found a detection limit for acetic acid of 5.3 µg/m3 (linear response between 50 - 650 µg/m, r=0.975)

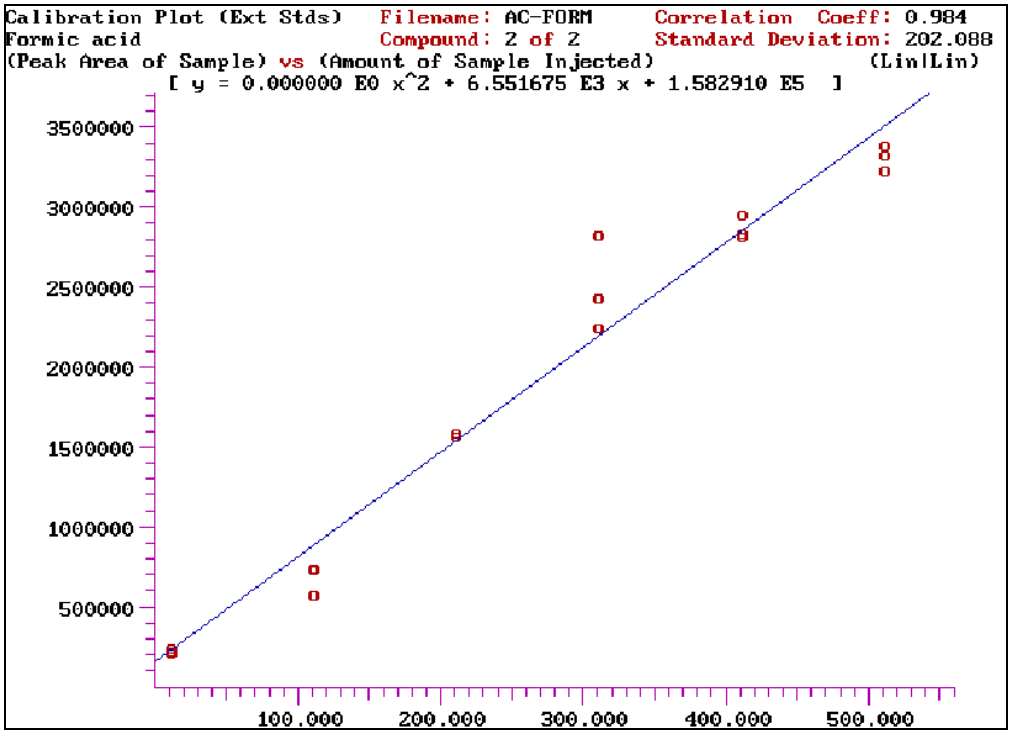

Figure 2: Calibration curve, formic acid

We also tested new SPME fibers, with different phases: polydimethylsiloxane/divinylbenzene (blue), carbowax/divinylbenzene (orange), Carboxen/polydimethylsiloxane (black), and the polyacrylate (white) we have been using until now.

All fibers were exposed to mixed standards of 200 µg/m3 of formic acid and 200 µg/m3 of acetic acid, followed by analysis by GC/MS. The result was promising, new fiber types like the polydimethylsiloxane/divinylbenzene has a much increased performance when collecting acetic acid, however, the Carboxen/polydimethylsiloxan fiber has far the best performance for both acetic and formic acid (fig. 3). The sensitivity is around 40 times better for acetic acid and 5 times better for formic acid than the old polyacrylate fibre.

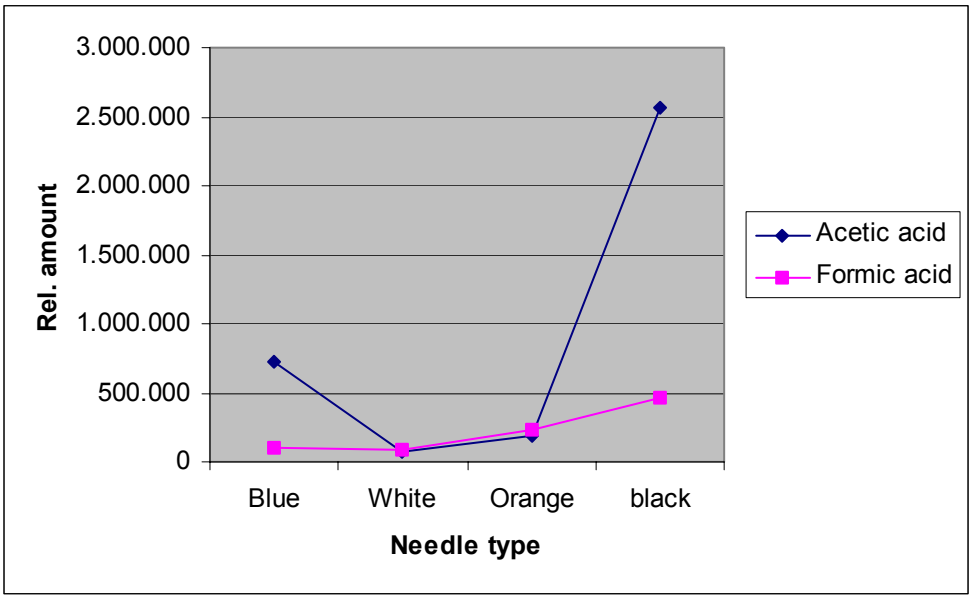

Figure 3:
Comparison between different phases: polydimethylsiloxane/divinylbenzene (blue), polyacrylate (white), carbowax/divinylbenzene (orange), and carboxen/polydimethylsiloxane (black).

2): Practical use of SPME sampling:

Being a fast and easy-to-use technique, we have found SPME sampling useful for acid emission detection from wood.

In recent experiments, we have been looking into the effect of reactive materials in showcases on the concentration of air pollutants. Our hypothesis is that the presence of museum objects reactive to air pollutants (e.g. lead objects reactive to acetic and formic acid) in a confined system like a showcase, may act as a scavenger, thus actually cleaning the air.

While the flux of pollutants emitted out of construction materials and onto the surface of the reactive museum objects may be more or less unchanged, the concentration of the pollutants in the case air may decrease to very low or not detectable. This may especially be the case where the reactive surface area of objects is large compared to the case volume and area of emitting construction material (many objects in a showcase) thus there's constantly a fast removal of pollutants from the air onto the object surface. If only the concentration of pollutants in the showcase air is used as a measure on the showcase air quality, one could be lead to a false sense of being secure, when measuring a low or no concentration of pollutants, e.g. with passive samplers. We propose, that determination of the area-specific emission rate of construction materials used in

showcases is a better measure of the "corrosion potential" of that case, than the concentration of pollutants in it.

We have demonstrated this by the following experiment:
In a steel emission test chamber of 0.227m^3, a more than 10 years old plank of oak was enclosed. The air exchange rate of the system was 1.5/24h, illustrating a semi-airtight showcase. Within the chamber the air were constantly mixed by a fan. The air used for ventilation was purified by activated charcoal and conditioned to 23°C and 45%RH. The plank had a surface area of 0.433 m^2, which gives a volume/area loading in the chamber of 1.9.

During the experiment the concentration of acetic and formic acid was monitored in the exhaust air from the chamber. During the first 21 days the concentration just increased constantly.

At the 21st day, a lead foil with a polished and clean surface was inserted into the chamber with the oak plank. This foil had a surface area of 0.143m^2, which is approximately 1/3 of the oak plank area.

Right after this the chamber concentration of acids off course decreased dramatic, as the chamber system had been disturbed by opening the chamber door to the ambient lab air. But the concentration of both acetic and formic acid stayed low, and actually continued to decrease for the next 60 days until the experiment was terminated (fig 4).

If we assume that the emission rate of acids from the wood was unchanged* it is obvious that the sudden fall in chamber air concentration means that almost all the emitted mass of acids is being used by reaction on the lead surface. This means that a high amount of pollutants take part of deteriorating reactions within the chamber (showcase) despite the low concentration of acids in the chamber air which we measured.

*) *Actually there is a fair chance that the emission rate from the wood would even increase during the described conditions. As the emission rate of a pollutant from a material is dependent on the difference in concentration of the pollutants over and below the material surface. When the surrounding air concentration drops, this difference increases, thus increasing the rate of emission.*

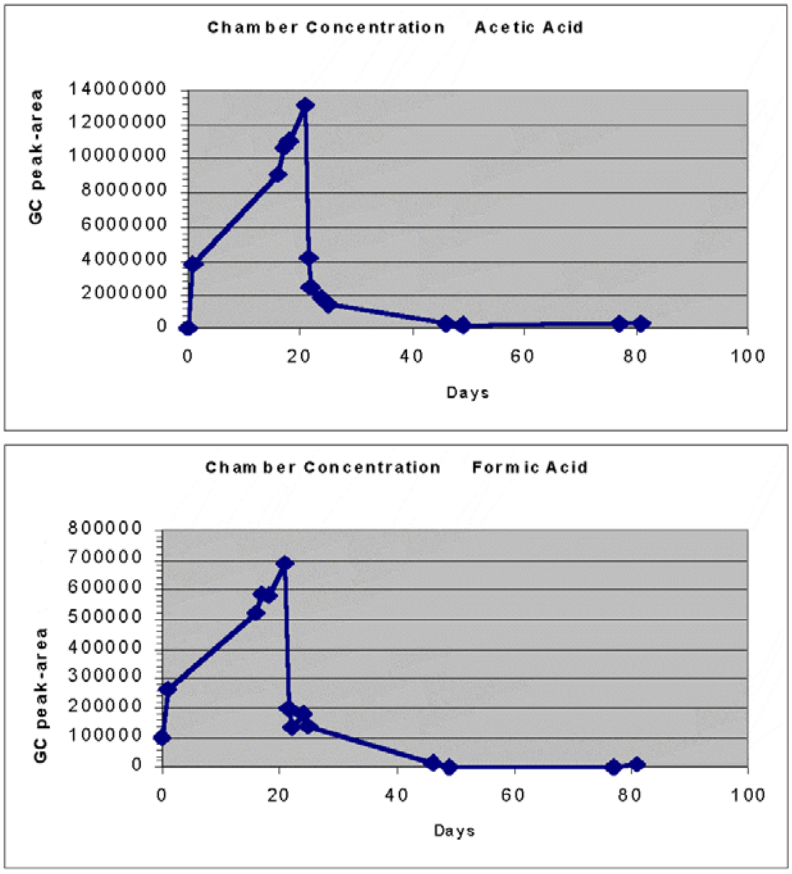

Figure 4: Decay curves for acetic acid (top) and formic acid (bottom) concentrations over 80 days in the chamber set-up. The lead foil was inserted on day 21.

Reference:

[1] Ryhl-Svendsen & Glastrup: "Direct measurements of acetic acid by SPME-GC/MS, and calculation of emission rates from emission chamber tests". Third Indoor Air Quality Meeting, Oxford Brookes University, 10th-12th July 2000, On-line: http://iaq.dk/iap/iaq2000/2000_14.htm

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Measuring particulates in historic buildings: A comparison of methodologies

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United Kingdom

In recent years, there has been an increasing amount of interest in the problem of dust deposition in museums. This has mainly been generated by large building projects, for instance at the V&A [Ford 1997], the British Museum [Kibrya 1999] and the Museum of Scotland [Eremin, Adams & Tate 2000]. These surveys have mostly been carried out using the "loss of gloss" method developed by Adams [Adams 1997], a very simple technique which measures the decrease in reflectance of ordinary glass microscope slides after exposure to a dusty environment.

During February and March 2001 I received a 'Sharing Museums Skills' award from the Millennium Commission, which enabled me to spend six weeks working with David Howell at the Textile Conservation Studio in Hampton Court Palace. I carried out a project to compare the "loss of gloss" method with direct measurement of the numbers of particles deposited on glass slides and the surface area covered, using a microscope camera and image analysis software. I also compared this technique with the number of particles captured using black sticky pads, which are used for mounting small objects for examination in the scanning electron microscope.

Glass slides and sticky pads in the Pages' Chamber, Hampton Court Palace

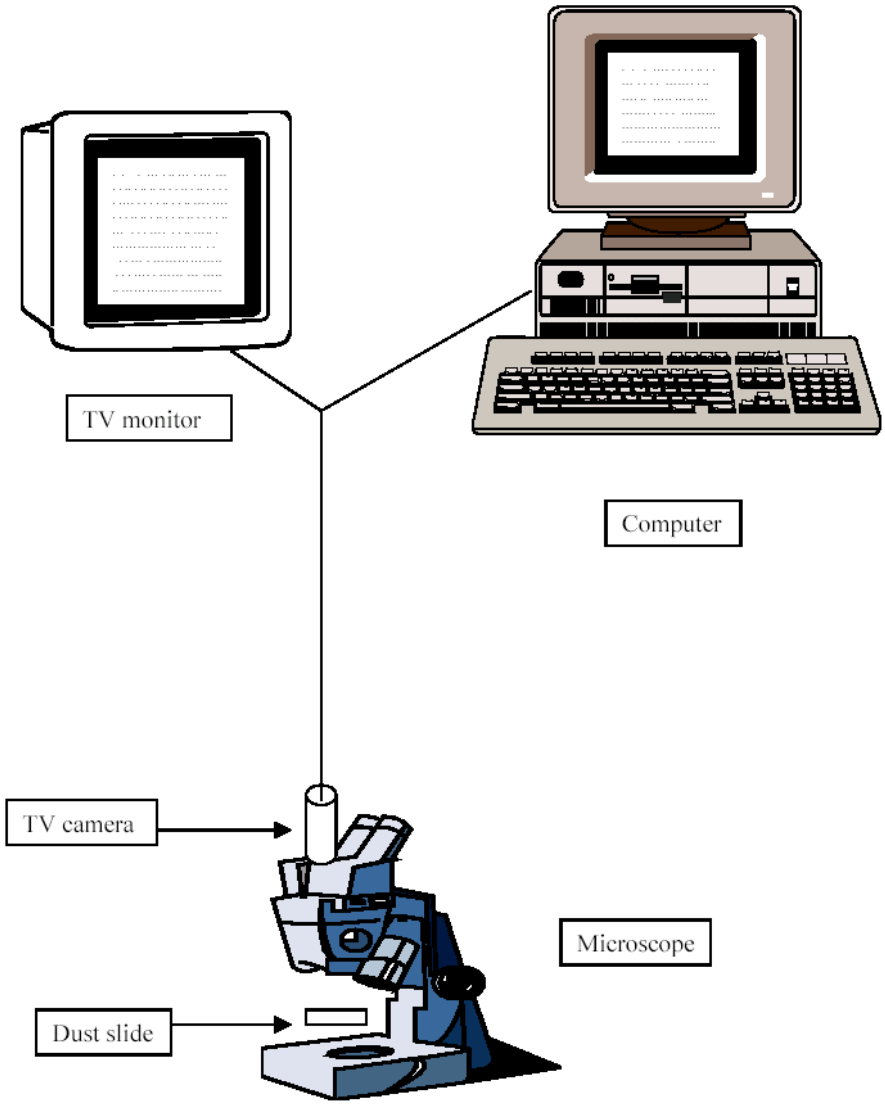
Five glass slides and five sticky pads were put out in each of four locations in Hampton Court Palace, and one slide and one sticky pad were collected each week. For both the slides and the sticky pads, the number of particles and area covered were measured using the microscope camera, and the decrease in reflectance of the slides was subsequently measured by Stuart Adams. The slides were standard 26 x 76mm glass microscope slides, while the sticky pads were double-sided self-adhesive carbon-coated pads, either 12 or 25mm diameter. The pads were adhered to 12 or 25mm aluminium stubs to facilitate handling, and were placed in wooden holders with holes drilled to accept the stems of the stubs.

For measurements on glass slides, a Nikon Labophot with a transmitted light base was used, with a x4 objective. The images were acquired with a Donpisha 3CCD colour vision camera module. For measurements on black sticky pads a Microvision MV120Z microscope camera was used, with a magnification of x240. This has an integral fibre optic illuminator which gives uniform vertical lighting, and is ideal for detecting light coloured particles on a dark background. With both cameras, the image was viewed on a TV monitor so that the area of interested could be identified and focused.

Image analysis was performed using IMAQ Vision Builder for Labview, version 4.0 This is a very versatile program which permits particles to be identified, counted, and their areas measured. It is also capable of discriminating particles on the basis of shape, so that, for example, fibres can be distinguished from other particles, although this was not done in these experiments. The analysis proceeds in several stages that can be individually selected and controlled before being incorporated into a procedure which runs automatically on the click of a button. These stages are:

1. Acquire new image.
2. Calibrate image – a 1mm graticule was imaged and its length in pixels was recorded. This calibration factor enables measurements to be reported directly in micrometres.
3. Extract colour plane – only the red part of the colour image was used, to improve discrimination of particles from the background.
4. Threshold – only objects falling within a certain range of brightness on the grey scale from 0 (black) to 255 (white) are recorded. After this operation, the image consists of black particles on a white background. Different settings were required for bright field (glass slides) and dark field (sticky pads) measurements. It was quite difficult to choose values which enabled the program to identify all the particles that could be seen on the TV without generating spurious images. This was more difficult for the sticky pads, because it is more difficult to distinguish dark coloured particles on a black background than light coloured particles on a bright background.
5. Particle filter – particles covering fewer than 3 pixels (smaller than 6 μm^2) are removed as these are mostly artefacts introduced by the thresholding step.
6. Look-up table: reverse – changes the image from black particles on a white background to white particles on a black background.

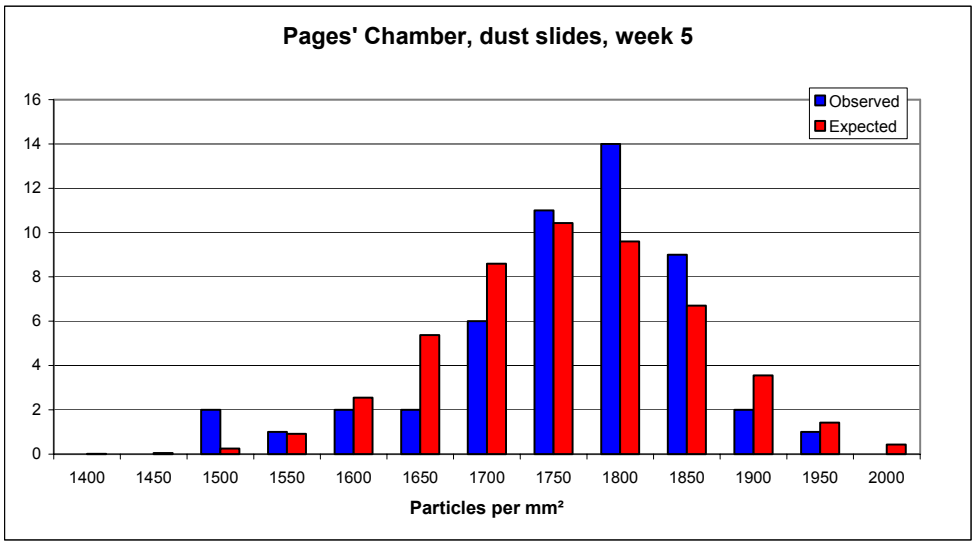
7. Image mask – the border of the image is removed as it contains white lines that confuse the counting process. The field of view was approximately 1mm².
8. Particle analysis – counts the number of particles and measures their areas. The data are transferred to Excel where the total area can be calculated and the particle size distribution plotted.



Schematic layout of equipment

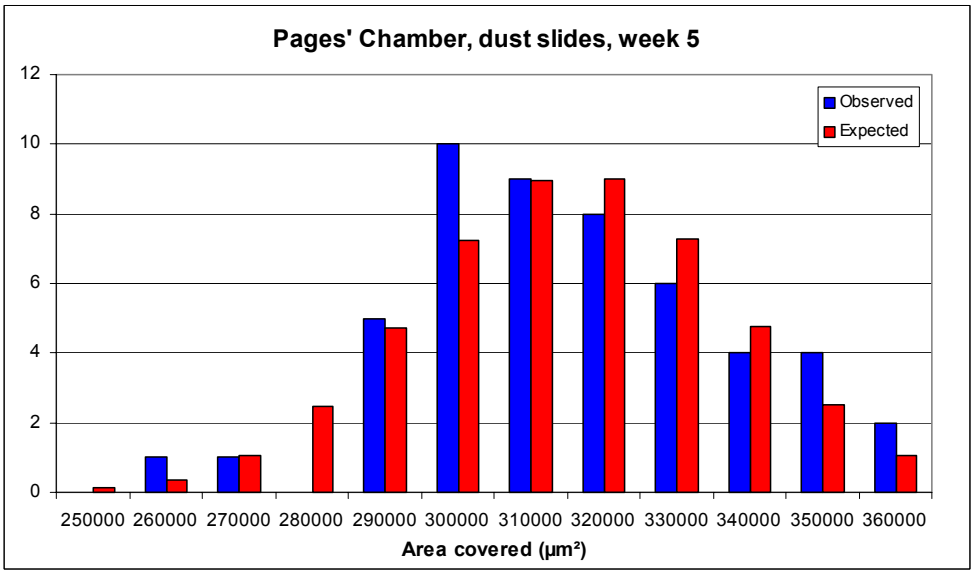
There was found to be considerable variation between readings, particularly when only a small fraction of the surface was covered (eg less than 1%). In order to obtain good statistics, 50 measurements were made for each slide or sticky pad. The glass slides were sampled at 5mm intervals in a 10 x 5 grid, so as to get good coverage of the whole

slide, while the sticky pads were examined more randomly, though trying to avoid overlapping fields as far as possible. It was found necessary to avoid the edges of the sticky pads because of finger marks which confused the image; it was also found that some of the sticky pads had been touched, making the readings unreliable.

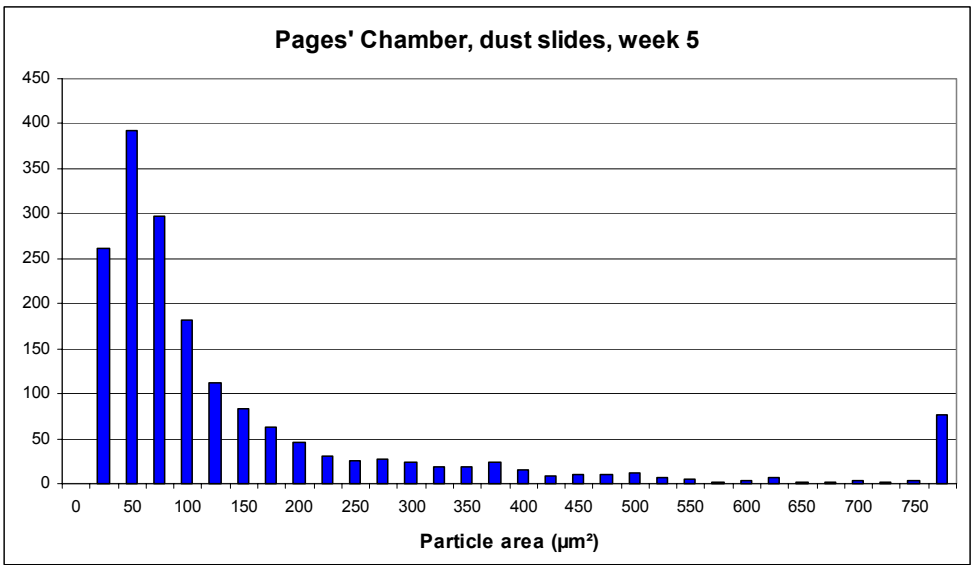


The results for both numbers of particles per square millimetre and total area covered show a reasonably good fit to a Gaussian distribution calculated using the means and standard deviations obtained from the data. The fit is not perfect, but nevertheless it is good enough to be able to say that both numbers and areas do follow Gaussian statistics.

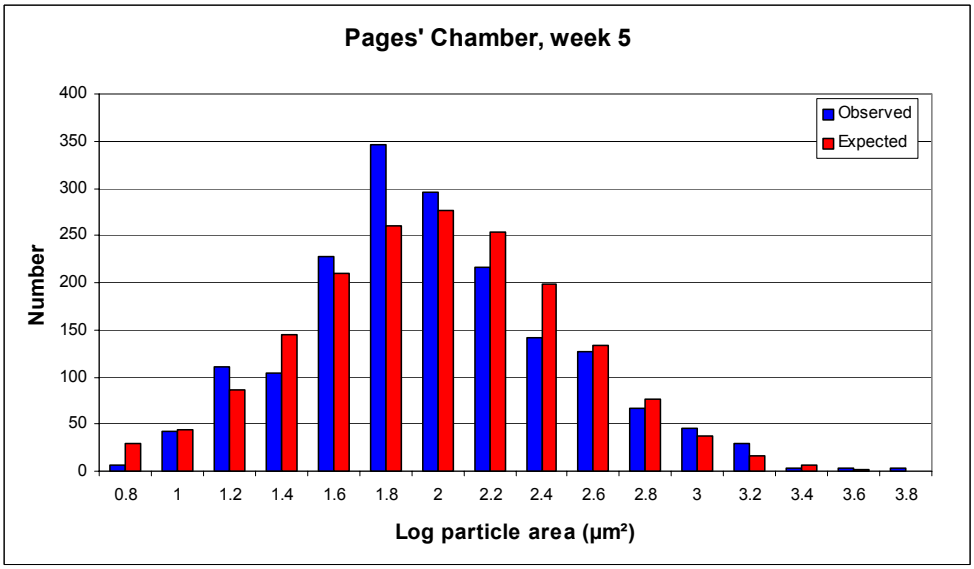
We can also look at the particle size distribution: it can be seen that the peak falls at about 50µm², but the distribution is very skewed to larger sizes. It is worth pointing out that most particles are larger than 10µm diameter, and in fact we do not measure



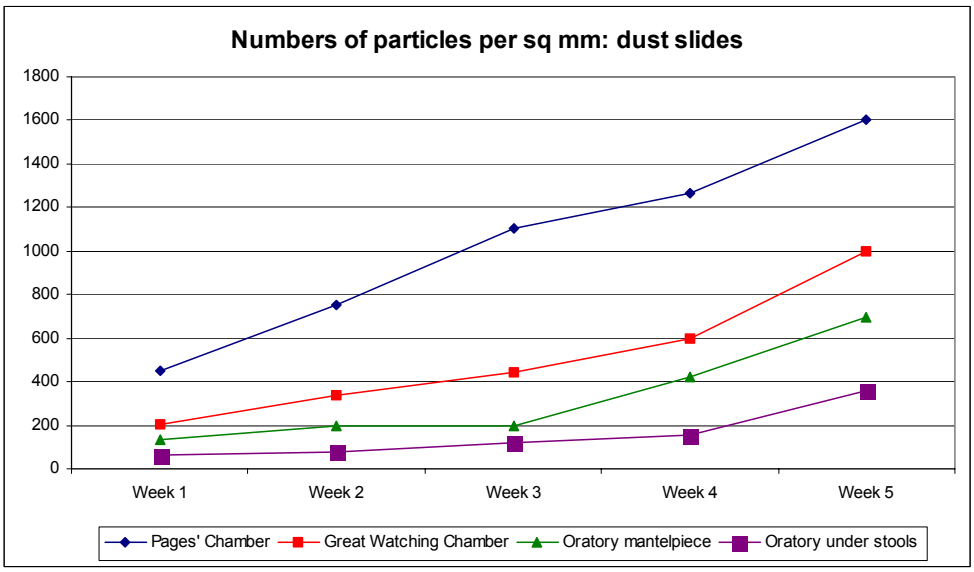
particles smaller than about 1.5µm diameter, so the particles which are of greatest significance for human health (< 1µm diameter) are not significant for soiling, and conversely, the particles which are significant for soiling are too large to be inhaled.



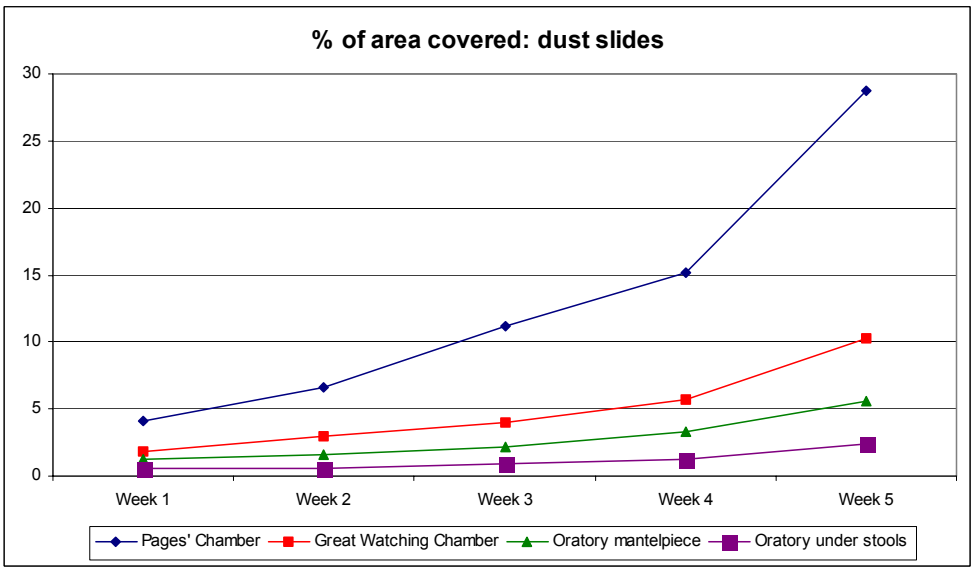
However, if the number of particles is plotted against the logarithm of the particle area, we can see that the data fit a Gaussian curve much more closely: this is a lognormal distribution. Such distributions are encountered in many natural phenomena, and occur when an effect is produced not by the addition of many small random effects, but by their multiplication. In this case, we can imagine that large particles are broken down into smaller ones by many successive impacts, so that while there are many small particles there is still a residue of larger ones [Limpert, Stahel and Abbt 2001].

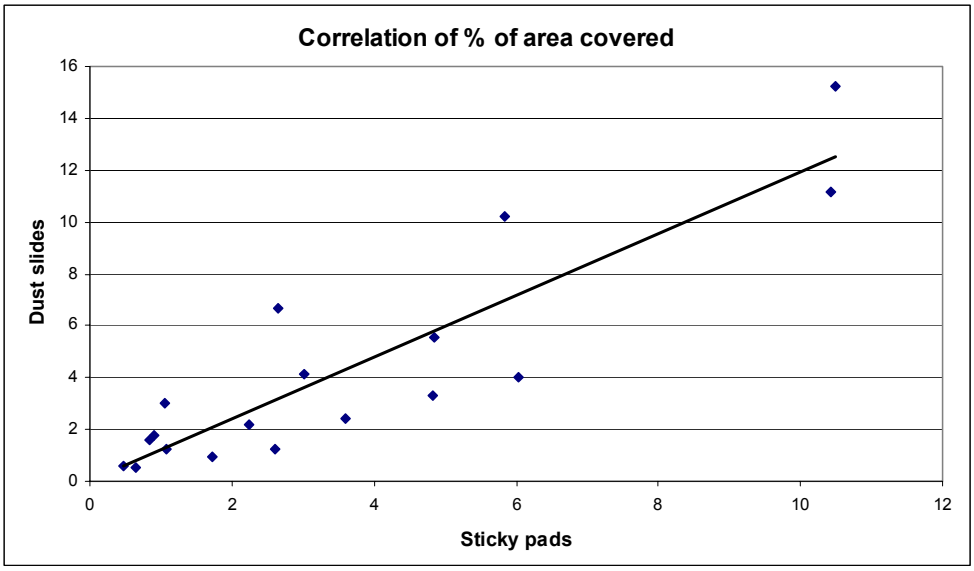


It can be seen that there is a steady increase in both the number of particles per square millimetre and the fraction of the surface area covered, and that there are clear differences between the different locations in Hampton Court. Only the results using the dust slides are shown, because, as explained earlier, the results from some of the sticky pads were unreliable because of finger marks on the surface. However, the trend of the results is the same.

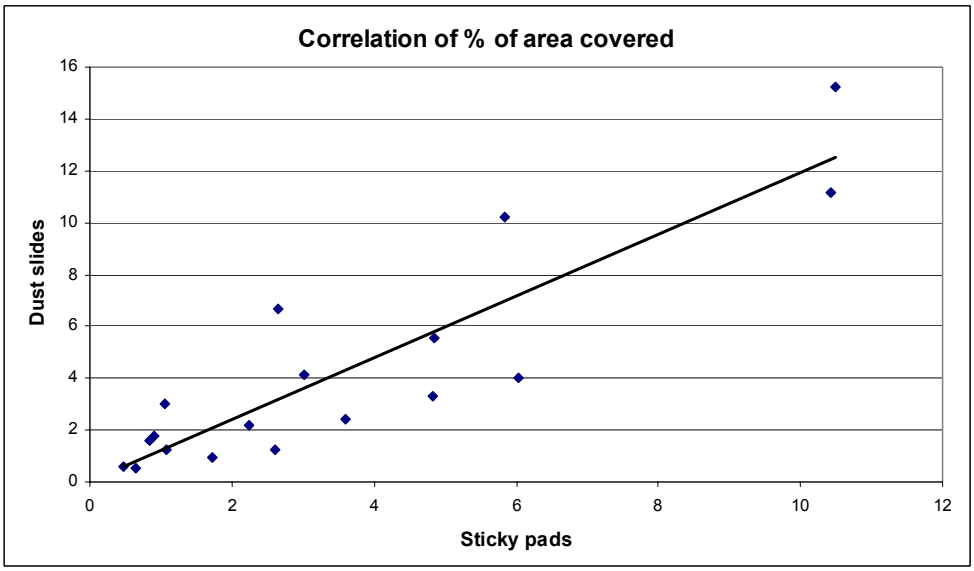


Consistently more particles are seen on the dust slides than on the sticky pads, and their average size is smaller. As explained above, this is because of the difficulty in discriminating small and dark-coloured particles against a black background. The end result is that the area covered as estimated from the slides is about 20% greater than that estimated from the sticky pads.



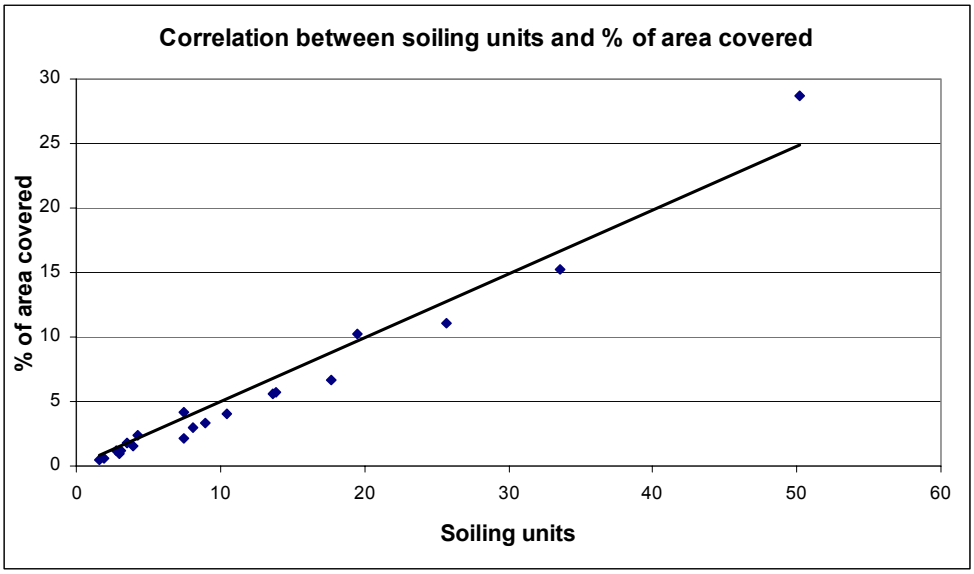


The results for the percentage of the area covered may be compared directly with Stuart Adams' "loss of gloss" measurements on the same slides – his results are expressed in soiling units, where 1 SU corresponds to a 1% decrease in reflectance.



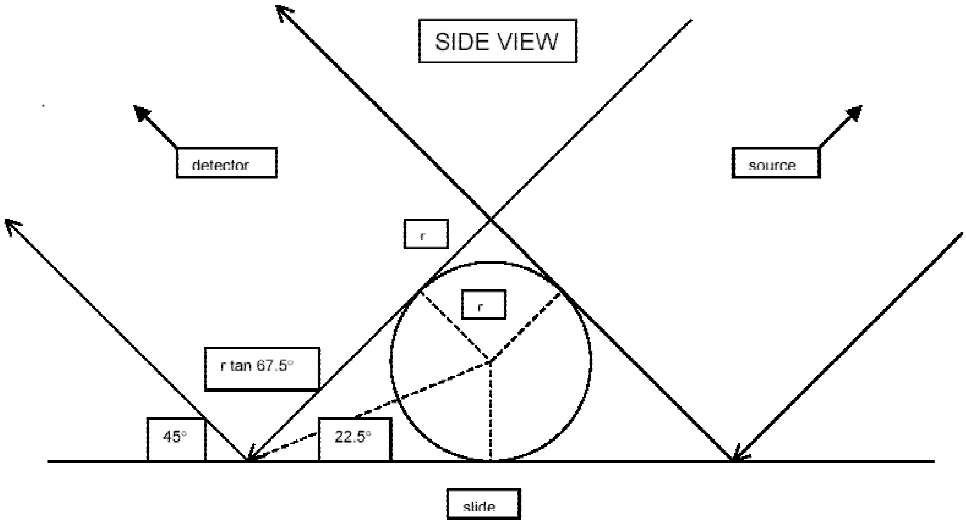
When we compare the figures for the percentage of area covered with the percentage decrease in reflectance, we again find a very good correlation, but curiously the number of soiling units is twice as large as the percentage of area covered. It seemed very hard to account for this, but following up a suggestion from Peter Brimblecombe, I looked at the geometry of the two measurement techniques. When the slides are examined with

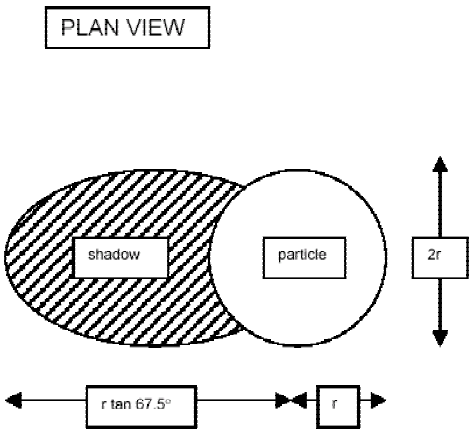
the microscope, the light is incident at 90° so the area of the shadow of the particle is the same as the its area projected onto the plane of the slide. In the reflectometer used to measure the decrease in reflectance, the light is incident at 45°, so the area of the shadow is not the same as the projected area of the particle. Instead, the area of the shadow depends on the shape of the particle. The relationship between the area of the shadow and the projected area of the particle can be worked out for a variety of shapes and orientations, but I will just look at the simplest case of a spherical particle.

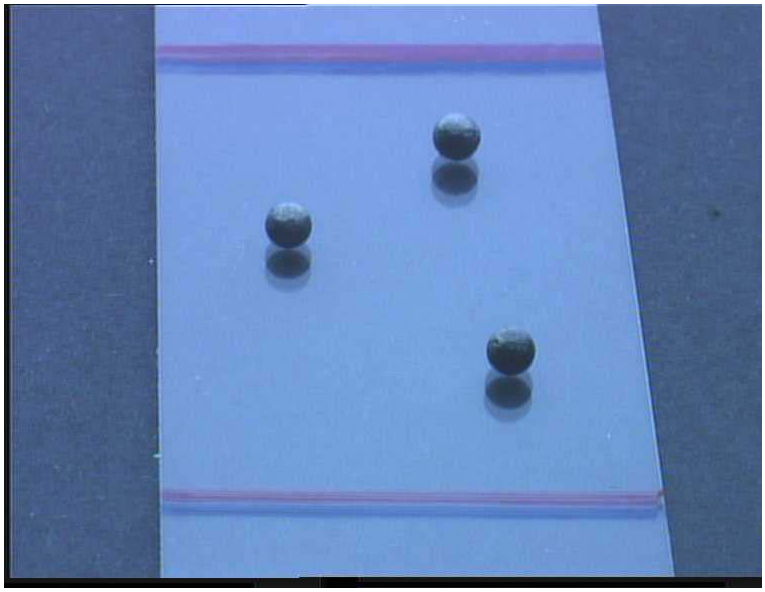


The geometry is not quite as simple as you might think, and I hope the situation is clear from the diagram below. The light is coming from the right at 45° to the plane of the slide. Some of the light is blocked by the particle before it is reflected from the slide and some is blocked after it is reflected. Some easy trigonometry shows that while the shadow cast by a spherical particle of radius r also has a radius of r when illuminated vertically, when the particle is illuminated at 45° it casts an elliptical shadow of length (r tan 67.5°) and width 2r. We also need to consider the light blocked directly by the particle, and together with the shadow the total area covered can be approximated by an ellipse of length r(1 + tan 67.5°) and width 2r. The area of this ellipse is $\pi \times r \times r/2(1 + \tan 67.5°)$, while the area of the circular shadow when the particle is illuminated vertically is πr^2, so the area of the elliptical shadow is approximately 1.7 times the area of the circular one. Similar calculations can be carried out for other shapes of particle in different orientations. These show, for instance, that for flat plates the area of the shadow when seen at 45° is only 0.707 of the area when seen vertically. The actual measured ratio will depend on the average shape of the particles, and may therefore vary from location to location, depending on the nature of the dust.

Dave Howell kindly carried out some experiments for me by placing some lead shot on a horizontal microscope slide, illuminating them at 45°, and photographing the shadows. It can be seen that the shadows do indeed have the shapes shown in the diagram, but in addition, there is a very clear reflection from the underside of the slide. Because the thickness of the slide is much greater than the diameter of a dust particle, this second shadow will be considerably displaced from the position of the particle. If this shadow is indeed measured by the reflectometer, it would explain why the area covered appears to be twice as large as when measured with vertical illumination.







Lead shot on a glass slide, illuminated at 45°

This is not to cast doubt on the value of the method, however, since it is quick and easy to carry out, and enables comparisons of the rate of dust deposition to be made between different locations. It can also be argued that viewing the slides at 45° is more closely related to the way in which dust is actually perceived in the real historic house environment. As every housewife knows, if you want to know how dusty a polished surface is, you look at it at an angle, not vertically!

I would particularly like to thank the Millennium Commission for giving me a 'Sharing Museum Skills' award so that I could carry out the work presented here, Amber Xavier-Rowe for encouraging me to apply for the award and English Heritage for giving me study leave, and Jenny Band of the Textile Conservation Studio at Hampton Court for agreeing to host me. I am also grateful to Dave Howell, Peter Brimblecombe, Young-Hun Yoon and Stuart Adams for their help and support throughout.

COMPARISON OF TECHNIQUES:

	Sticky pads	**Dust slides**	**Reflectance**
Angle of incidence:	90°	90°	45°
Field of view:	Rectangular 1.26 x 0.96 mm	Rectangular 1.19 x 0.91 mm	Elliptical ~ 10 x 14 mm
Area analysed:	1.21 mm^2 x 50 = 60.5 mm^2	1.08 mm^2 x 50 = 54 mm^2	110 mm^2 x 3 = 330 mm^2

Sticky Pads Area covered $(\mu m)^2$ = 143 x number of particles
Dust slides Area covered $(\mu m)^2$ = 94 x number of particles

Number of particles (dust slides) = 1.73 x number of particles (sticky pads)
Area covered (dust slides) = 1.20 x area covered (sticky pads)

% of area covered (dust slides) = 0.5 x Soiling Units

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Measuring soiling on vertically mounted textiles

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United Kingdom

Abstract

Work in progress is described for simulating the soiling of vertically mounted textile surfaces. A sealed chamber has been constructed, and different textiles exposed to a standard test dust. Colorimetric comparisons are made of samples before and during exposure and results correlated to the integrated particulate concentration of the chamber.

Results will be linked to other methods of measuring particulate soiling with the eventual aim of developing a predictive tool for soiling of vertically mounted textiles.

Next pages:
Slides from presentation:
Experimental setup, Experimental substrates, The dust, Grimm monitor, Experimental chamber, Measurement parameters

The full presentation (21 slides, approximately 0.6 MB files) can be viewed on the Internet: http://iaq.dk/iap/iap2001/2001_19.htm

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Experimental setup

- Aim - to accelerate soiling of different textile types
- Use of standard dust
- Within enclosed chamber

Experimental substrates

- As light as possible
- no surface finishes
- range of textures
- four cottons & two silks selected

The dust

- Standard test dust selected with good contrast
- Ashrae 52/76
  - 72% mineral
  - 23% carbon
  - 5% cotton linters

Grimm monitor

Experimental chamber

Measurement parameters

- Yxy co-ordinates
- converted to ΔE
- Relative to white background tile

Airborne dust in a museum environment

Anne Lisbeth Schmidt[1], Pernille Bronée[1], Kåre Kemp[2], and Jes Fenger[2]
The National Museum of Denmark[1]
National Environmental Research Institute, Denmark[2]

Abstract

Air pollution in Copenhagen
Urban air pollution in Denmark has been systematically monitored since the early 1980es. In most cases The National Environmental Research Institute has carried out the measurements in collaboration with local authorities.

Like in most of the industrialised world the nature of air pollution has changed radically during the recent decades. Previously, high concentrations of sulphur dioxide and soot due to combustion for space heating dominated the urban atmosphere. The use of cleaner fuels and improved technology (including transition to district heating based on combined heat and power production) has by and large solved this problem. Today the dominant source of urban air pollution is the increasing traffic. In spite of catalytic converters on petrol driven cars the level of NO_2 has not been reduced, since the ozone available for the oxidation of the primary pollutant, NO largely determines it. Furthermore an increasing number of diesel driven vehicles emits organic compounds and small particles.

This change in composition of the urban air pollution has primarily had an impact on human health. But also the degradation of materials and objects, many of which are placed in museums, is influenced.

The National Museum
Like many other major Danish museums the National Museum in Copenhagen is situated in the city centre, surrounded by trafficked streets. The narrow Stormgade has an average daily traffic of 16,000 vehicles (85% cars, 15% heavy vehicles), and the street canyon effect enhances the impact of pollution. In the immediate vicinity of the museum runs one of the busiest, broader streets in Copenhagen, H.C.Andersens Boulevard, with a daily average traffic of 62,000 vehicles (90% cars, 10% heavy vehicles).

The National Museum is housed in a large building square, with the oldest part dating back to 1684. In 1743-44 the buildings were reconstructed and until 1780 the so-called Prince's Palace was used as residence for the royal family and court. From the middle of the 19th century the Prince's Palace has housed the National Museum. In 1929-38 the museum was reconstructed and received its present outer appearance.
As a part of an extensive renovation in 1989-91 the heating system was changed and a stationary air conditioning system was installed in part of the building complex.

The ethnographic collections

For the newly restored air conditioned exhibition areas at the Ethnographic Treasure Rooms about 10,000 objects from the museum's Ethnographic Collections were prepared at the Department of Conservation during 1991-1998.

Ethnographic objects often consist of many different organic and inorganic materials (fur, feather, textile, plant material, pigments, metals etc.) and thus have very large surfaces where dust easily deposit. Many objects have been exhibited since the last rebuilding of the museum and had not been cleaned during the intervening more than 50 years.

Such objects are soiled with a greasy greyish or black layer which is difficult to remove by means of dry methods (vacuum cleaning, compressed air, erasing). Methods using a wet media for instance water, ethanol or white spirit, depending on the material to be treated, had often to be applied to get the wanted cleanliness - wanted both for aesthetic reasons and because dust generally is assumed to accelerate material degradation. Painted objects and other fragile surfaces were often impossible to clean and thus had to be left untreated.

Maybe too late the question arose: were the newly cleaned objects now more susceptible to degradation in the new exhibition or would they have been more protected with the old layer of dirt? Scanning the conservation database it is obvious that the main cause for the treatment of the objects has been to remove secondary soil from the surface of the objects. As secondary soil is understood dust or soil originating from the storage or exhibition at the museum. Primary soiling, on the other hand, from the original use and handling of the object - for example grease, soot or blood - is normally considered as important evidence and is therefore not removed.

Analyses of the dust layer

In 1995 the Department of Conservation initiated an examination of the nature of the old dust layers on various objects. The analyses were based on scanning electron microscopy, transmission microscopy, elementary analysis (EDAX) and pH-measurements. The test material was either collected on a filter connected to a micro vacuum cleaner or at adhesive stubs pressed to the surface of the soiled object (Hersoug et al, 1995). These analyses surprisingly suggested that dust could act as a buffer against the impact of new dust and aggressive air pollutants. The very limited analyses concluded that the dust layers consisted of non-agressive pollutants with a pH of 7.6.

Monitoring of dust

In the winter 1998 a further study of the properties of the particulate pollution, which is deposited on the exhibited objects today, was initiated. Two rooms in the museum were investigated: One room in the newly restored Ethnographic Treasure Rooms has no windows and 80% recirculation with fresh air intake through filters. The other room has windows facing a courtyard and the above-mentioned heavy trafficked street Stormgade and has no ventilation. In this room silver exhibits from the Medieval Collections are on display.

In both rooms dust were collected by so called streakers in two size fractions above and below 2 mm respectively. The concentration of NO_2 was determined with passive

filter samplers placed adjacent to the streakers and outside the window in the room without ventilation.

In the room, where the Medieval Collections are exhibited, it is necessary to consider the protection of the silver objects. Installation of an effective ventilation system is greatly to be preferred, but hardly likely. Instead other measures must be taken - e.g. lacquering of the metal surfaces or installation of sealed showcases equipped with absorbents. So far the Department of Conservation surveys these exhibitions closely as regards the silver objects.

Measurements

The streaker sampler is a small aerosol collector with low power consumption and a low noise level. That makes it suitable for i.a. indoor measurements. The aerosols are separated in two size fractions by means of an impaction stage. Particles having an aerodynamical diameter > 2 μm are collected on an impaction stage with a greased polycarbonate film as collection surface. The fine fraction (<2μm) is collected on a polycarbonate filter. It is possible to collect the dust on up to 60 discrete spots on each film/filter (Kemp and Møller, 1981).

During the project period we changed the exposure time in a scheme between one day and one week for each sample. As it was a pilot project we did not know the concentration levels to be expected. With the long exposure time better detection limits could be achieved, while the short times could give information about the changes depending on time.

The samples were analysed by means of Proton Induced X-ray Emission Spectroscopy (PIXE). It is a multi-element analysing method, which gives determination of all elements having atomic number greater than 13 (aluminum). In the present samples detection limits below 0.1 ng/m3 were achieved for many elements. The streaker measurements were conducted in parallel in the two rooms mentioned. Impregnated filters for collection of NO2 (nitrogen dioxide) were placed close to the aerosol samplers and in addition one was placed just outside the window in the unventilated room. Collection was done in one-week periods during the sampling period.

The results are compared to data collected by the air quality network in Copenhagen (Thomsen, 1999; Kemp and Palmgren, 2001). One station, at street level, is placed on H.C. Andersens Boulevard about 500 m from the museum. Another station, at roof level, is placed on the H.C.Ørsted Institute at University of Copenhagen about 3 km from the museum.

Results

Twenty elements were found in concentrations above the detection limits. These elements may not as such constitute any risk for the exhibits, but they can be used as indicators for the type of pollution that enters the building and that may be produced within the building. Typically particles produced by combustion are mainly found in the fine fraction, while particles from mechanical processes are predominant in the coarse fraction.

Elements as e.g. S, V, Ni and Pb in the air are mainly of anthropogenic origin. Whereas Si, Ca, Ti, Fe and Sr originate primarily from windblown dust and dust from buildings. If we look at the average distributions for these elements a marked difference is found between the two rooms (Fig. 1).

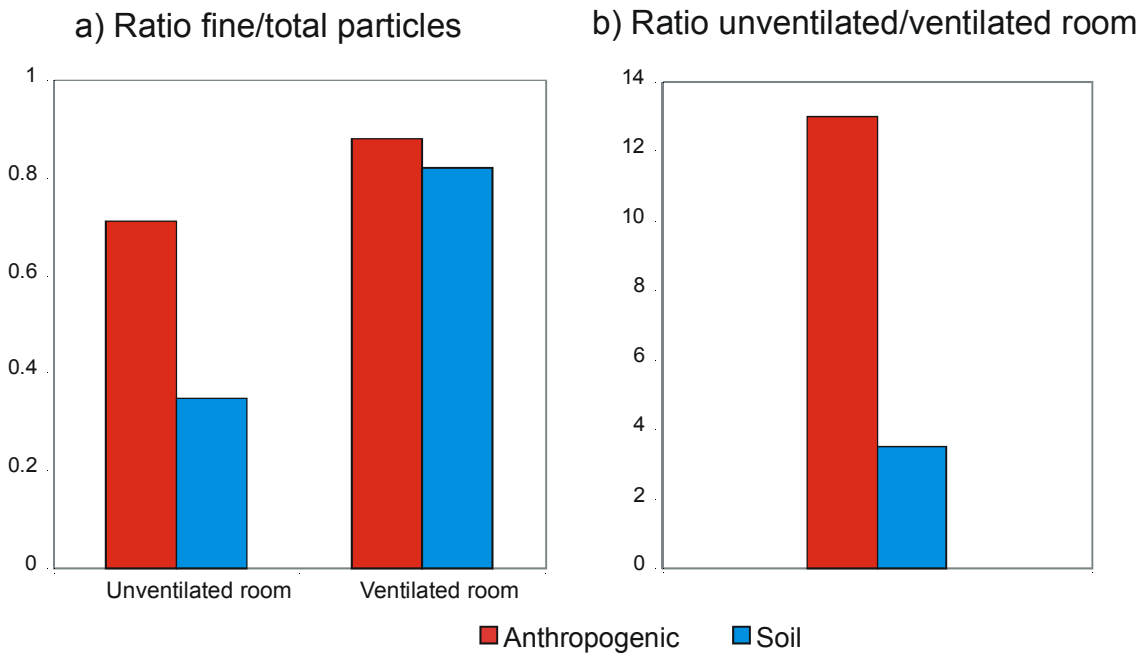

Figure 1: Average results for "anthropogenic" and "soil" elements.

a) Average ratios between the mass found in the fine particles fraction and the mass found in both fractions

b) Ratio between the concentrations in the ventilated and unventilated room

In the unventilated room (with windows) 2/3 of the anthropogenic particles are found in fine fraction, while only 1/3 of the soil particles are in the fine fraction. Almost all of the coarse particles are removed by the ventilation system. It may be unexpected that more than 90% of the anthropogenic particles are removed by the ventilation system while only 2/3 of the soil particles are removed. An explanation may be that there is a "production" of particles that are not efficiently removed by the recirculation in the ventilation system. These productions may be caused by particles raised by the traffic of museum guests and emission from newly painted surfaces. These properties can be illustrated by the measured time series for some “typical” elements (Fig. 2).

For sulphur there is an almost perfect match between the three time series with fixed ratios 1:5:75 between the concentrations at the three locations. The difference between the three locations is much more pronounced for Ca.
In the general higher concentrations are found in the ventilated room, with an exception on December 7, which was a Monday when the museum is closed.

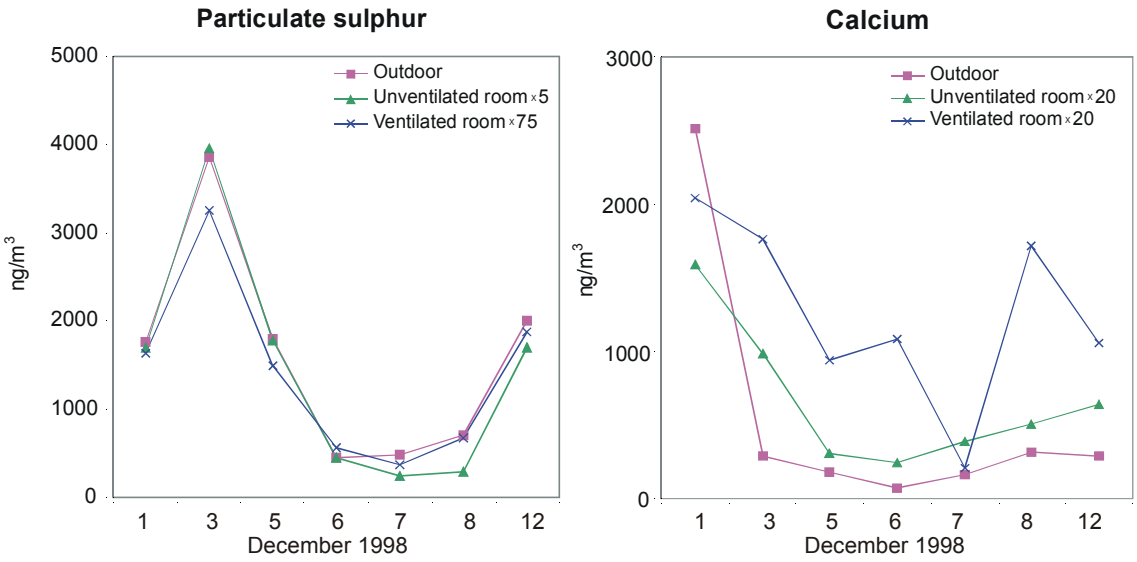

Figure 2: **Time series for the total concentration of "anthropogenic" particulate sulphur and the "soil" element calcium.**

The ratios between the NO_2 concentrations at the different locations (Fig. 3) were almost the same during the sampling periods. The two outside locations, just outside the window at the museum and the roof station, were almost identical. The concentration was reduced with a factor of two in the windowed room, while it was 1/3 in the ventilated room.

Conclusions

The outdoor pollution is a main source for fine particles of "anthropogenic" origin in both rooms. The ventilation system removes more than 98% of these particles. The ventilation system is less efficient for locally produced fine particles than the "natural" ventilation in the medieval room. Gases are removed less efficiently than particles. Potential harmful gases (both of local and outdoor origin) and fine particles of local origin may contribute to the soiling and decomposition of the exhibits, even with an efficient ventilation system.

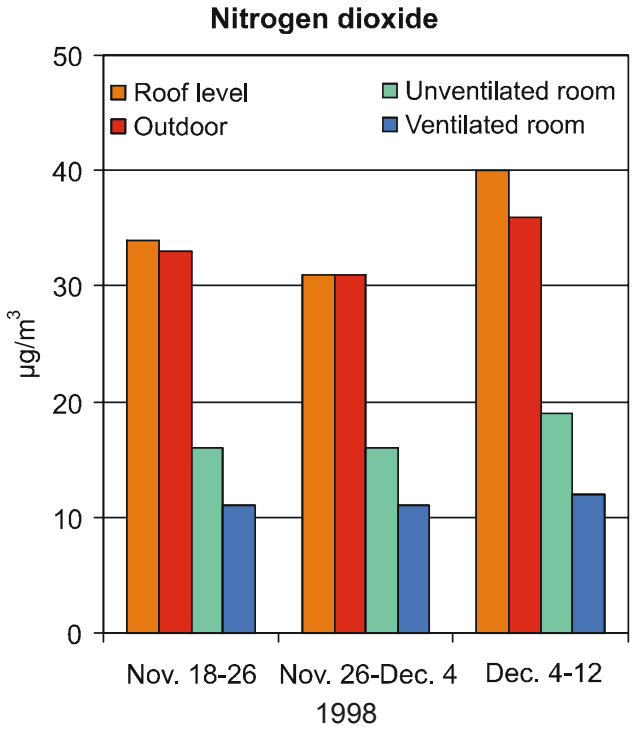

Figure 3: Nitrogen dioxide measured in the two rooms compared to two outdoor locations

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Field determination of particle filtration efficiency

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Abstract

Cultural institutions in urban areas, especially in New York City, have to remove large quantities of fine particulate and gaseous compounds that are generated in the outdoor air by traffic and other air pollution sources. In order to purge agents from the air stream, these institutions expend considerable resources to design and install high-efficiency particulate filtration systems and in some cases, chemical filtration systems.

These systems displace a considerable amount of valuable floor space, their operation consumes energy and replacement materials are costly. Additionally, filter efficiencies are only certified for an individual filter, not a series of filters mounted within a fan system. As a result, facility operators have no means to verify if their filtration systems are achieving the efficiencies specified or advertised to other institutions.

The purpose of this study was to develop a field protocol to determine the true efficiency of filtration equipment while in operation in three New York City cultural institutions.

The ASTM D 2986-95a and ASHRAE 52-2P laboratory methods for filtration efficiency were adapted for field use in two separate scenarios. The first was to determine particulate sizing and concentration of ambient particles existing upstream and downstream of the filter bank utilizing an aerodynamic particle counter and sizer (fig 1). The second was to test efficiency by artificially generating small monodispersed polystyrene latex spheres (PSL) at 0.6μm and 1.2μm. These particles were generated by emulsion polymerization with an Atomizer Aerosol Generator (fig. 2).

Results revealed mean efficiencies in 3 separate HEPA equipped filter banks to be 90%, 77% and 82% for total ambient particle counts. The causes for the difference in expected and realized efficiency was investigated and it appeared, that in most cases, the decrease in efficiency could be contributed to bypass of particles around and between the installed filters in the bank and not as a result of individual filter performance. Thus, it is clear that a standardized test method should be developed and implemented to verify that installed filtration systems are achieving design intent during normal operating conditions. New particulate generation and detection technology has advanced to a level to allow verification in a field environment.

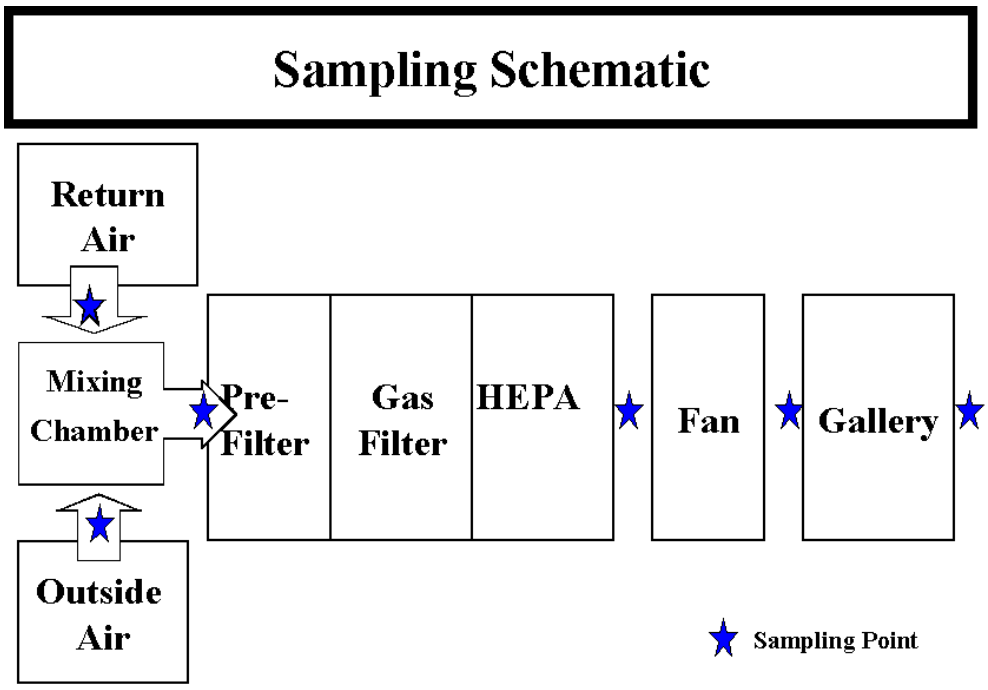

Figure 1: Schematic diagram of measuring sites, upstream and downstream from filter bank

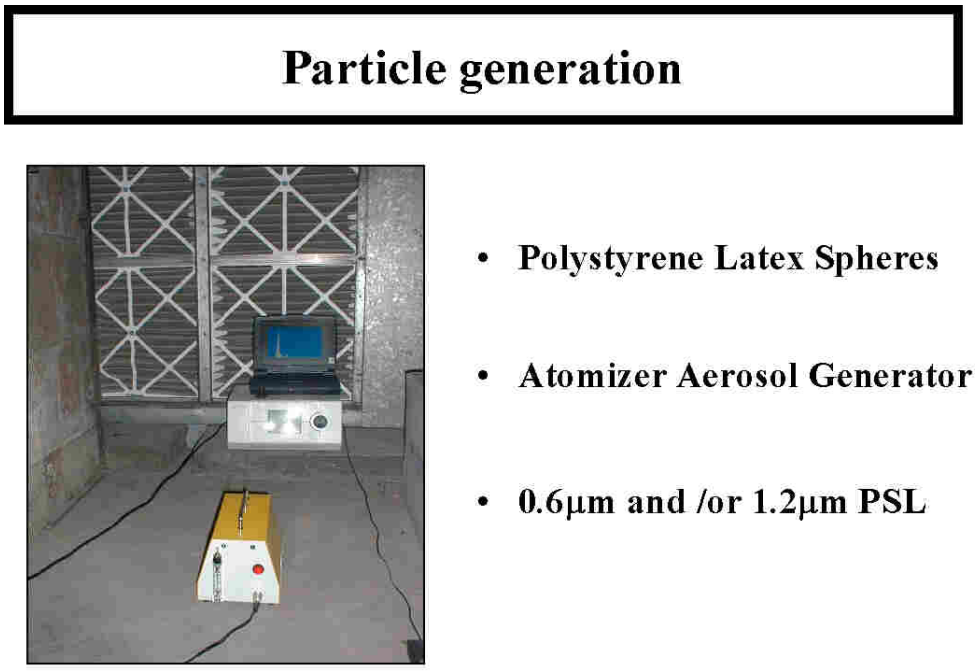

Figure 2: Generation of small monodispersed polystyrene latex spheres

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Analysis of volatile organic compounds in indoor air

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Analysis of Volatile Organic Compounds in Indoor Air

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INTRODUCTION

- Volatile organic compounds (VOCs) are a cause of concern for human health due to their increased presence in the indoor environment.
- They are responsible for a phenomenon known as the sick building syndrome (SBS).
- Air monitoring is being used to assess indoor pollution.
- Solid phase extraction (SPE) procedures are used extensively for trapping and removing VOCs from indoor air.

AIM

- The aim of this work is to develop a method for the determination of the VOCs toluene , ethylbenzene , o-xylene and cumene (TEXC) in air. VOCs are extracted using solid phase extraction cartridges and the extracts are then analysed and quantified using a gas chromatograph with flame ionisation detection (GC-FID).

SPE Procedure

- The cartridge was conditioned and washed with 3 mL of methanol.
- The system was then equilibrated with 3 mL of 50:50 solution methanol:water.
- 3 mL of a standard solution containing 100 µg mL^{-1} of all analytes in methanol:water were loaded onto the cartridge.
- The analytes were eluted with 3 mL of dichloromethane (DCM) into a 5 mL volumetric flask.
- 100 µL of a dichlorobenzene (DCB) external solution was added to the extract giving a DCB concentration of approximately 80 µg mL^{-1}.
- The extract was analysed and quantified using GC-FID.
- The cartridges that were used during the SPE method were Waters C18 cartridges and Anasorb CSC coconut shell charcoal cartridges.

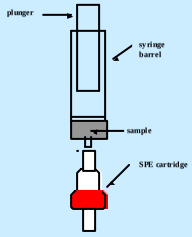

Figure 1 : A schematic diagram of the SPE apparatus.

INSTRUMENTATION

PERKIN - ELMER 8500 Gas Chromatograph
PERKIN - ELMER GP - 100 graphics printer

RESULTS AND DISCUSSION

- Standard solutions of different concentrations containing all analytes and DCB in DCM were prepared in order to investigate the linear calibration range. The GC response was found to be linear up to 400 µg mL^{-1}.
- The minimum elution volume of DCM required to desorb all of the analytes from the sorbent was found to be 3 mL.

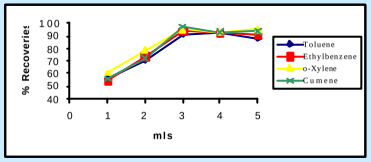

Figure 3: Recoveries for analytes using Activated Charcoal cartridges in different elution volumes.

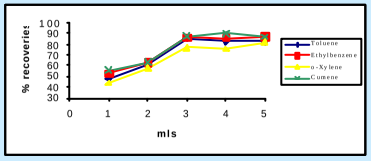

Figure 4: Recoveries for analytes using C18 cartridges in different elution volumes.

- The SPE method was found to be precise at the optimum conditions by performing 4 replicate extractions.

Table 1: Recoveries for all analytes using C18 cartridges.

Analytes	% Recoveries			
Toluene	91	92	88	92
Ethylbenzene	93	91	90	94
o-Xylene	98	91	96	96
Cumene	92	92	96	94

- Cartridges were found to be reliable even after repeated use. Recoveries of approximately > 90 % for each analyte were obtained for cartridges used 10 times previously. After each experiment cartridges were cleaned by washing with DCM.
- Stability of the VOCs retained in the SPE cartridges was investigated over time. Immediately after preparation, the analyte recoveries were approximately 95 % and 85 % for C18 and activated charcoal cartridges, respectively. In room temperature significant loss of analytes was obtained for both cartridges. Even when the cartridges were stored at -4°C, recoveries of approximately 60 % were obtained after 30 days suggesting that new methods of storage will have to be developed.

Table 2 : Recoveries of analytes for cartridges stored in -4°C.

	% Recoveries					
	C18 Cartridges			Activated Charcoal Cartridges		
Analytes	after 1 day	after 2 days	after 30 days	after 1 day	after 2 days	after 30 days
Toluene	92	88	56	72	64	47
Ethylbenzene	95	90	63	76	68	51
o-Xylene	99	95	65	60	58	43
Cumene	100	96	75	80	73	60

Table 3 : Recoveries of analytes for cartridges stored in room Temperature.

	% Recoveries			
	C18 Cartridges		Activate Charcoal Cartridges	
Analytes	after 1 day	After 2 days	after 1 day	after 2 days
Toluene	85	81	54	48
Ethylbenzene	89	83	58	57
o-Xylene	93	91	45	44
Cumene	94	92	62	60

CURRENT AND FUTURE WORK

- The SPE procedure developed in this work is currently being assessed for analytes in the vapour phase. An environmental chamber has been constructed to obtain VOC contaminated air, and an active sampling pump is used to drew the air over the C18 and activated charcoal cartridges.
- Remedial technologies are also being addressed. New crystalline silicates are being designed , synthesised and tested for the removal of VOCs from contaminated air.

IAP Copenhagen 2001
The National Museum of Denmark
Meeting Programme

Thursday, Nov. 8th

Opening of IAP 2001

Welcome, Start of meeting
Morten Ryhl-Svendsen, *National Museum of Denmark*

Welcome
Mads Chr. Christensen, *National Museum of Denmark*

Opening presentation

Microclimate: A difficult variable in museums
Dario Camuffo, *National Research Council, Italy*

Session on Air Physics and Chemistry

Surface reactions of deposited NO_2 in the museum environment
Peter Brimblecombe, *University of East Anglia, UK*

Copper and lead corrosion in carbonyl environments
Jean Tétreault, *Canadian Conservation InstituteThursday, Nov. 8, continued*

Measurement of case exchange rates and the use of such measurements
Simon F. Watts, *Oxford Brookes University, UK*

Non-spherical holes and wavy tracer gas decay curves. A comparison of theory and real life with respect to leakage of display cases
Frank J. Ligterink, *The Netherlands Institute for Cultural Heritage*

The ventilation of enclosures to reduce internally generated pollutants and simple techniques to measure air exchange rates within enclosures: report on progress to date
Andrew Calver, *Museum of London, UK*

Session on Communication and IAQ problems

The conservation of ceramics contaminated with acid induced salts: necessitiy of a multi-disciplinary approach
Lieve Halsberghe, *Luxenburg*

Clearing the air: communicating air quality issues to museum staff and responding to external accusations at the National Gallery of Australia
Janet Hughes, *National Gallery of Australia*

Session on Communication and IAQ problems - cont'.

"Indoor Environment Engineering for Heritage Conservation": Report from a workshop at the Clima2000 Conference
Liveo de Santoli, *Dept. Fisca Tecnica, Italy*
(REHVA - Representatives of European Heating and Ventilating Associations)

The *IAQ in Museums Website*: Future directions
Morten Ryhl-Svendsen, *National Museum of Denmark*

Friday, Nov. 9th

Session on Pollution Monitoring and Control

A study on monitoring in the Germanic National Museum
Arnulf v. Ulmann, *Germanisches Nationalmuseum*

Acid sampling collection rates
Claire Watt, *University of Strathclyde, Glasgow, Scotland*

Development of a damage assessment dosimeter using piezoelectric quartz crystals coated with egg based films
Marianne Odlyha, *Birkbeck College, UK*

The protection of Cultural Heritage and the use of diffusive sampling
Franco De Santis, *CNR – Istituto Inquinamento Atmosferico, Italy*

Emission of organic acids from wooden construction materials in a small test chamber; preliminary results of optimisation of the Solid Phase Micro Extraction technique
Maarten van Bommel, *Netherlands Institute for Cultural Heritage*

Recent improvements in SPME-GC/MS detection of acetic and formic acid in air
Jens Glastrup, *National Museum of Denmark*

Indoor Air Quality in Japanese museums
Chie Sano, *National Research Institute for Cultural Properties, Japan*

Session on Particulates in Museum Air

Airborne Dust in the Museum Environment
Anne Lisbeth Schmidt, *National Museum of Denmark*
Kåre Kemp, *National Environmental Research Institute, Denmark*

Measuring particulates in historic buildings: a comparison of methodologies
Barry Knight, *English Heritage, UK*

Measuring soiling on vertically mounted textiles
Richard Kibrya, *The Victoria & Albert Museum, UK*

Particle Profiles and Filtration Efficiency in Museums
William Esposito, *Ambient Group, USA*
(ISIAQ - International Society of Indoor Air Quality and Climate)

End of IAP2001

See you at the next IAP Working Group Meeting:

"Indoor Air Quality in Museums and Historic Properties"
University of East Anglia, United Kingdom

April 28th - 29th, 2003