Microclimate Indoor Monitoring in Cultural Heritage Preservation (MIMIC): the development of a piezoelectric quartz crystal-based damage dosimeter

Marianne ODLYHA*, Tim PADFIELD, Morten RYHL-SVENDSEN, Franco De SANTIS, Victoria SMITH, Linda BULLOCK, José Antonio RUIZ HERNANDO and Jaap J. BOON

Summary

In the previous ERA (Environmental Research for Art Conservation, contract no. EV5V-CT94-0548) project, paint-based dosimetry was shown to work. The degree of physicochemical damage in the paint resulting from exposure of these dosimeters for a selected time and in various galleries was found to be consistent with the indoor environmental conditions at these sites. In the MIMIC project (Microclimate Indoor Monitoring in Cultural Heritage Preservation, contract no. EVKV-CT-2000-00040) further exposure of paint dosimeters is made at galleries and historic castles in Northern and Southern European locations where indoor environmental conditions are also monitored in terms of relative humidity, temperature, light, and pollutants (NO₂, NOₓ, SO₂, ozone, HONO and HNO₃). Furthermore, in the MIMIC project the concept of paint dosimetry is extended to incorporate coatings (egg tempera, varnish) applied to 10MHz piezoelectric quartz crystals. An array of these coated crystals is then used to continuously monitor the physicochemical change in the coating, involving mass change, in terms of frequency shift in the crystals. Coated crystals also undergo calibration in a test rig with controlled environmental conditions.

Introduction

The project ‘Microclimate Indoor Monitoring in Cultural Heritage Preservation’ (MIMIC) contract no. EVKV-CT-2000-00040 is funded by the European Commission Environment Programme, Area 4.2 ‘Protection, conservation and enhancement of cultural heritage’ of the Key Action ‘The City of tomorrow and Cultural Heritage’.

Assessment of damage to indoor cultural heritage, in particular by pollutants, is a major and growing concern for curators and conservators. Our aim is to provide early warning systems both to assess damage and estimate threshold values at which it occurs, initially in environments where air quality and microclimatic anomalies have been characterised. Damage dosimeters (paint-based) have been developed in the previous ERA project (VAN DEN BRINK, 2000; BACCI, 2000; ODLYHA, 2000). The novel contribution in this project is their further calibration, using known and varying levels of pollutants, and then extension of their capabilities to provide rapid in-house evaluation procedures using piezoelectric quartz crystal (PQC) technology. Preventive conservation practice, where this is not already in place, will be introduced to sites which are heavily visited and which are repositories of our cultural heritage. These will include Northern and Southern European locations with different levels of environmental control and where problems have already been recognised.

Complementarity of the project

The participating organisations are:

– Birkbeck College, University of London, United Kingdom (BBK, coordinator)
– CNR – Instituto Inquinamento Atmosferico (IIA) and Istituto di Fisica Applicata ‘Nello Carrara’ (IFAC) Italy
– El Alcázar, Spain (ALC)
– The National Trust, United Kingdom (NT)
– The National Museum of Denmark (NMD)
– FOM Institute voor Atoom en Molekuulfysica – AMOLF, The Netherlands (FOM)

Each participant is presented in detail on the MIMIC project website: http://iaq.dk/mimic

Overall complementarity of the consortium

While BBK, CNR, and FOM will provide instrumentation and chemical analysis, in regard to the evaluation of the paint dosimeter, development of the piezoelectric quartz crystal-based dosimeter, and sites for monitoring will be provided by NT, ALC, NMD. Besides these sites, additional locations have been chosen, such as the Uffizi Gallery in Florence, Italy.

At NT, NMD, and ALC an interaction of preventive conservation will take place, in that NT and NMD will assist and provide guidance to ALC in environmental monitoring. Furthermore, NT will provide a course for housekeeping staff at ALC in preventive conservation. NMD collects and organises data from the environmental monitoring at each location, and together with data from the chemical analysis, all data will provide the ground for an overall analysis and damage assessment of the different sites.
The conservation of cultural heritage for sustainable development

Complementarity of locations
NT and NMD provide a site each within a typical Northern European climate. These include the following: Sandham Memorial Chapel, United Kingdom, and one of the rooms in The National Museum of Denmark. In contrast to these, El Alcázar, Segovia, and the Uffizi Gallery provide locations in typical Southern European climate. A further complementarity of the four locations is, that while Sandham Memorial Chapel and El Alcázar represent semi-rural environments, the National Museum of Denmark and the Uffizi Gallery are located in urban areas.

Objectives
The main objective of the project is to provide a system for continuous monitoring of damage caused by conditions in the environment surrounding works of art, and particularly paintings, in museums and historic buildings.

This will be approached in stages, namely:
– Preparation and exposure of paint-based damage dosimeters to selected indoor cultural heritage locations for defined periods of time.
– Monitoring of the environmental conditions at the selected locations: relative humidity, temperature, light and pollutant levels (NO₂, NOₓ, SO₂, O₃, HNO₂, HNO₃) for more than twelve months, in order to quantify the indoor environmental conditions.
– Calibration of the paint dosimeters to various dosage levels of light and selected pollutants (NO₂) at controlled temperature and relative humidity in ageing chambers.
– Preparation of new dosimeters involving application of organic coatings (egg tempera, resin mastic) to piezoelectric quartz crystals. Use of these initially as (VAN DEN BRINK, 2000) passive samplers for monitoring damage. Correlating shifts in frequency with chemical change in the coating involving change in mass (BACCI, 2000) to provide a measure of damage continuously in terms of frequency shifts due to chemical changes in the coating.
– Calibration of coated (egg tempera, resin mastic) piezoelectric quartz crystals, to controlled and defined periods of exposure to relative humidity and NO₂ providing conservators with a capability to evaluate the cumulative risk of contaminants via a direct read-out, as opposed to sophisticated chemical analysis.

Furthermore, a final objective of the project is to introduce preventive conservation practice to sites where it is not already in place.

Background
In the previous ERA project (Environmental Research for Art Conservation, EV5V-CT94-0548) a ‘mock’ painting or paint dosimeter was proposed as a damage dosimeter. By measuring physico-chemical changes or damage in the paint, after exposure to an environment for a set period of time, ranking of sites was possible, and this was in accord with the level of observed environmental control.

Paint dosimeter
In the ERA project the paint dosimeter consisted of twelve differently pigmented egg tempera strips (9x65 mm) mounted with double-sided adhesive tape onto a black background and a backing of a polymethylmethacrylate support plate. The composite was contained in an aluminium frame 14x19cm (VAN DEN BRINK, 2000). Both the egg tempera preparation and the design of the dosimeter were slightly amended in the MIMIC project. The egg tempera strips in the MIMIC project include the following:
– Unpigmented
– Lead white (Aldrich)
– Smalt (Kremer)
– Lead chromate (Aldrich)
– Alizarin (Acros)
– Mastic (Roberson X thin)
– Azurite (Kremer)
– Basic copper carbonate (Aldrich)

Accelerated and natural ageing

In the ERA project, paint dosimeters were exposed at locations in the Clore Gallery (Tate), London; the Rijksmuseum, The Netherlands; El Alcázar, Segovia, Spain; Uffizi Gallery, Italy, and Sandham Memorial Chapel, National Trust, England, Wales and Northern Ireland. The paint tempera was also exposed to accelerated light ageing under controlled conditions (Tate Conservation Dept.). The physicochemical changes in the paint were measured for both accelerated and natural ageing by thermal, spectroscopic and mass spectrometric measurements (VAN DEN BRINK, 2000; BACCI, 2000; ODLYHA, 2000). The latter provides information at the molecular level on chemical changes. Table 1 illustrates the extent of change observed at the sites. Areas where chemical change was high and the thermal stability properties had changed most were denoted by the number 6; areas where chemical change was minimum and the change in thermal stability low were denoted by number 1. Thus, the numbers are allocated for ranking and do not represent real values. Thermal stability is a measure of the temperature at which the onset of thermal degradation of the sample begins or at which a selected fraction of the material has reacted when the sample is heated. The chemical change measured for accelerated ageing for some of the temperas (e.g. smalt tempera) was found to vary in a systematic manner with ageing. This allowed some correlation of change with days of light ageing. It was found, however, that in some cases the chemical change was greater than the most severe case of accelerated light ageing (64 days at 18,000 lux). Further experiments using accelerated ageing at various conditions of RH, light and pollutants need to be performed to consider the synergistic action of environmental factors.

Besides the thermal stability, indices of damage assessment were also obtained from a number of analytical techniques. The extent of colour change and the change in reflectance for each paint dosimeter were determined by visible reflectance spectroscopy using fibre optics – FORS (BACCI, 2000), chemical changes at the molecular level were determined by mass spectrometry (VAN DEN BRINK, 2000), and mechanical changes by thermomechanical analysis. An example of a set of damage assessment indices obtained from the various techniques are given in Table 2 for Sandham Memorial Chapel data. Once again these are expressed in terms of high (6) or low (1) amount of change in the physicochemical properties:

Project stages

The stages of the MIMIC project are:

– Using paint dosimetry to assess damage of selected, different environments. Damage assessments are compared to the indoor air quality at each site, determined by ‘traditional’ means.
– Using piezoelectric quartz crystal technology for damage assessment, first with crystal arrays modules registering cumulative damage, and secondly by using microprocessor controlled crystal modules with continuous recording and logging of data.

Paint dosimetry

In the MIMIC project, the paint dosimeters are exposed at the four locations for one year, with analysis performed after the first six months, and again after twelve months. The tasks involved in this are divided among the scientific partners of the MIMIC project team in the following order:

BKK: Preparation of paint dosimeters. Determination of the thermal stability of paint.
FOM: Chemical analysis of paint by mass spectrometry.
CNR Monitoring of pollutants and accelerated ageing of paints by pollutants. Measurement of colour change of paint.

Table 1. Thermal Stability Index for accelerated light-aged and naturally aged paint (smalt) dosimeters exposed at various sites. Legend to damage: 6 = high; 1 = low.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Light-aged (64 days)</th>
<th>Alcazar</th>
<th>Rijksmuseum Nightwatch room</th>
<th>Rijksmuseum Store</th>
<th>Sandham Memorial Chapel</th>
<th>Tate (Clare Gallery)</th>
<th>Uffizi (Leonardo’s Room)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smalt</td>
<td>6</td>
<td>5</td>
<td>3</td>
<td>2</td>
<td>6</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>
The conservation of cultural heritage for sustainable development

Results from the first six months of exposure of dosimeters in two locations in El Alcázar are shown in Table 3.

Description of microclimate at sites
Parallel to the paint dosimetry, the indoor air quality is assessed for each location by measuring the relative humidity, temperature, and light levels once per hour. This is performed by climate sensors connected to battery operated data loggers. The pollution levels are determined by passive samplers, provided and analysed by CNR (IIA). In this way monthly averages of NO₂, NOₓ, SO₂, O₃, HNO₂, HNO₃ are determined. In Figure 3 this is exemplified by charts of the pollution levels at the National Museum of Denmark (urban environment) and El Alcázar (semi-rural).

Continuous damage assessment, piezoelectric quartz crystal technology
Following the damage assessment by paint dosimeters, the indoor environment will then be assessed using coated piezoelectric quartz crystals (PQC) (HLAVAY, 1977; HIERLEMANN, 1995). Uncoated PQCs have a particular oscillation frequency, in this case 10MHz. Coatings on the quartz crystal surface will reduce this frequency, and chemical changes in the coating accompanied by changes in mass will cause additional frequency shifts. During exposure to any aggressive environment, the cumulative degree of damage to the coating can be evaluated.

At each of the selected sites, an array consisting of eight crystals with coatings of egg tempera and resin mastic varnish are exposed for one month. The array is mounted in a box with a protecting cover, which allows the box to be posted back and forth for analysis at BKK. The oscillation frequency is determined for each crystal before and after exposure.

Following this, complete modules of crystals mounted to real-time reading instruments will be installed at the sites. These instruments provide data logging facilities for up to one year of continuous measurements of the accumulating damage to the quartz crystal coatings.

Currently, calibration of the crystal arrays are in progress, as well as exposure at the first couple of sites. Figure 4 illustrates the response profiles of coated PQCs to nitrogen dioxide under lab conditions (dry and 50% RH). The measurements were made by Dr. K. Pratt (Chemistry Dept, University College London, University of London).

Conclusions so far
Paint dosimeters, being responsive to several environmental factors, allow the synergistic effects of air pollutants, light exposure, temperature, and moisture to be measured.

The measured damage can be used to rank different sites, and the obtained data gives insight into the type of damage that is dominant at each site. The level of damage is influenced by the level of environmental control at each site.

Table 2. Indices of damage assessment of paint dosimeter exposed at Sandham Memorial Chapel, UK, obtained from various analytical techniques.

<table>
<thead>
<tr>
<th>Sample:</th>
<th>ΔE</th>
<th>ΔR</th>
<th>TS</th>
<th>MS</th>
<th>TMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smalt</td>
<td>5 / 6</td>
<td>5</td>
<td>6</td>
<td>6</td>
<td>4 / 5</td>
</tr>
</tbody>
</table>

ΔE = Colour change (CIELAB); ΔR = Reflectance change; TS = Thermal stability; MS = Mass spectrometry; TMA = Thermomechanical analysis
Legend to damage: 6 = high; 1 = low

Table 3. Damage assessment by paint dosimetry in two locations of the El Alcázar castle: the Cord Room, and the Military Museum. Damage in the Cord Room is dominated by light. Lead chromate in lead chromate tempera is particularly sensitive to light ageing.

<table>
<thead>
<tr>
<th>Tempera Paint</th>
<th>Location</th>
<th>ΔE (Colour change)</th>
<th>Thermal stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead chromate</td>
<td>Cord Room</td>
<td>6</td>
<td>–</td>
</tr>
<tr>
<td>Lead chromate</td>
<td>Military Museum</td>
<td>3</td>
<td>–</td>
</tr>
<tr>
<td>Smalt</td>
<td>Cord Room</td>
<td>–</td>
<td>6</td>
</tr>
<tr>
<td>Smalt</td>
<td>Military Museum</td>
<td>–</td>
<td>2</td>
</tr>
</tbody>
</table>
Dosimeters provide a means for evaluating the urgency of preventive measures, and make it possible to answer the question: ‘Is it necessary to react, if so, when and how’.

**References**


**Acknowledgements**

MIMIC acknowledges the support of the European Commission DGXII ‘Protection and Conservation of European Cultural Heritage’.

**Marianne Odlyha**

Birkbeck College, University of London
Gordon House, 29 Gordon Square,
London WC1H OPP, United Kingdom
Email: m.odlyha@bbk.ac.uk

Manager of the University of London Service in Thermal Methods since 1988. Originally trained as a solid state chemist, she specialised in pigment and binding medium characterisation at the Doerner Institute, Munich, Germany, and was employed at the Courtauld Institute of Art in London (1988/89). Research has focussed on the application of thermal methods to characterisation of artists’ materials and effects of conservation treatment. This has resulted in over 60 publications in refereed journals, book chapters and lectures at international meetings and EU Advanced Study Course on Deterioration of Collagen-Based Historical Materials. She has been involved in three other EU projects: Coordinator of SCICULT Scientific Analysis of Cultural Objects, Coordinator of ERA Environmental Research for Art Conservation and participant in the Microanalysis of Parchment project.

**Franco De Santis**

Consiglio Nazionale delle Ricerche
Istituto Inquinamento Atmosferico
Via Salaria Km 29.3 CP10,
00016 Rome, Italy

**José Antonio Ruiz Hernando, Victoria Smith**

El Alcázar
Plaza Reina Victoria, Eugenia s/n,
40003 Segovia, Spain

**Linda Bullock**

National Trust
36 Queen Anne’s Gate,
London SW1H 9AS, United Kingdom
Tim Padfield, Morten Ryhl-Svendsen
National Museum of Denmark,
Conservation Department
PO Box 260, Brede,
DK-2800 Kongens Lyngby, Denmark

Jaap J. Boon
FOM Institute for Atomic and Molecular Physics
Kruislaan 407,
1098 SJ, Amsterdam, The Netherlands