Microclimate Indoor Monitoring in Cultural Heritage Preservation MIMIC (EVK4-2000-00040)

EC 5th framework : Subsection 4.2.1

Improved damage assessment of cultural heritage

Alcázar Segovia  Cord room

National Museum Denmark  Room 134
http://iaq.dk/mimic

webpage coordination & translation by Eliseo de Pablos, Spain.
“Virgin and Child”
Tüchlein by Pordenone

C.1496-1539

Circle indicates position of dosimeter.
Innovative Tools used in MIMIC project

1. Quartz crystal microbalance (array of coated piezoelectric quartz crystals)

2. Small framed palettes (based on ERA paint dosimeters) containing spray-coated metallic strips: 2 egg tempera and 2 resin mastic
How does the QCM function?

Piezoelectric quartz crystal

Electrodes are connected to an oscillator and AC voltage; the crystal starts to oscillate at its resonance frequency (10MHz)

Oscillation is very stable.

If rigid layer is deposited, resonance frequency will decrease with mass

High sensitivity and real time monitoring of mass (ng)
Rationale for selection of coatings

- **Egg tempera**: systematic response to light and differential response to site exposure.

- Loss of cis-unsaturation (left) and oxidation of the egg lipids (broadening of carbonyl)

Chemical change measured by FTIR.
FTIR Egg Control (crystal arrays and small palettes)

Light ageing

Red = control
Blue = L08
Purple = L16
Black = L32
Control egg tempera stored in anti-corrosion bag at 5°C
Change in cis region with time
**Rationale for selection of resin mastic**

- *Resin mastic*: mastic showed systematic behaviour on accelerated light ageing.
- Oxidation [left broadening of CO] and cross-linking (right) (Theodorakopoulos, 2005)

Chemical changes identified by ATR/FTIR reflectance
FTIR Mastic control (crystal arrays and small palettes)

Purple = Control
Site exposure
Blue = direct sunlight 12 hrs
Red = Chiswick (70 days)
Black = British Library (after 189 days)
Work Packages

**WP1&2** Environmental monitoring *El Alcázar, Segovia*, *National Museum of Denmark, National Trust (England, Wales and N.Ireland), and IIA (Rome, Italy)*

**WP3** Preparation and calibration of coated dosimeters *Birkbeck College (BbK), QuartzTec, UCL(Chem)*

**WP4** Accelerated ageing (light, pollutant) and analysis *Birkbeck College, CNR-IIA, FOM (Mass Spec), Winngate (UK) (X-ray surface analysis)*

**WP5** Integration of climate, dosimeter, and chemical data (all partners)
**WP1 & 2** Environmental monitoring and Processing of Climate data (Grand Unified MIMIC Data Base “GUMD”)

<table>
<thead>
<tr>
<th>PQC array</th>
<th>Start date</th>
<th>End date</th>
<th>No. Days</th>
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<th>T _av</th>
<th>T _max</th>
<th>T _min</th>
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<td>26.8</td>
<td>30.2</td>
<td>22.1</td>
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<th>T variations</th>
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<td>4,1-6,0C</td>
<td>&gt;8,0C</td>
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<td>30</td>
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<tr>
<th>RH _av</th>
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<td>49.5</td>
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<td>10,1-15,0%</td>
<td>&gt;25,0%</td>
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<td>18</td>
<td>12</td>
<td>2</td>
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<table>
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<tr>
<th>TWPI</th>
<th>Lightdose (kluxhrs)</th>
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<td>19</td>
<td>22.1</td>
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Pollutant dose (μg/m³)hrs

<table>
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<tr>
<th>Dose SO\₂</th>
<th>Dose O₃</th>
<th>Dose NO\₂</th>
<th>Dose NO\x</th>
<th>Dose HNO\₂</th>
<th>Dose HNO\₃</th>
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<tr>
<td>736.8</td>
<td>4281.6</td>
<td>13473.6</td>
<td>28492.8</td>
<td>7490.4</td>
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**Preservation Index (PI) values, in unit “years”,** shows the combined effect of T & RH on the chemical decay rate of vulnerable organic materials

**Time Weighted PI (TWPI)** is an average of changing PI values over time

TWPI values dosimeter exposure.

14°C, 40%RH = 124 Years

20°C, 50%RH = 44 Years (heat for human comfort lowers TWPI)

28°C, 70%RH = 10 Years

(http://www.climatenotebook.org)
WP1 & WP2  

Sites: TWPI (RH, T), light, ozone  
(April to Dec 2001)

Highest values
O$_3$
ALCMM
ALCC
(16-33 ug/m$^3$)

TWPI
SAC, ALC

Light
NMD_V ALCC
WP1 & WP2

$\text{NO}_x$, $\text{NO}_2$, HONO, $\text{HNO}_3$

$[\mu\text{g/m}^3]\text{hrs}$ (April to Dec 2001)

Highest values

$\text{NO}_x$, $\text{NO}_2$

$\text{NMD134}$

$\text{HNO}_3$

$\text{SAC}$

HONO

$7 \mu\text{g/m}^3$

$\text{NMD134}$
WP 3

1. Preparation of *tempera* & *mastic coatings* Melinex, steel & PQC arrays  (Dr.B.Ormsby & N.Wade)

2. *Design of cell for PQC arrays* (8). Adaptation of QuartzTec instrumentation

3. *Laboratory calibration of PQC arrays* in test rig using QTS-2 with controlled gas flow and RH.

4. Design of protocol for transport & site exposure

**Outcome**: Paint, palette (coated metal strips) & piezoelectric quartz crystal dosimeters. Cells for PQC arrays.
Innovative tool

PQC arrays

Damage dosimeters function either as passive samplers interrogated at monthly intervals (top left) or as continuous data loggers (below)

continuous data logger QTS-3

7cm x 5cm

22cm x 14cm
Damage dosimeters as passive samplers interrogated at selected intervals and frequency shifts measured back in laboratory

\((f/F)\) Mastic for cumulative exposure (days)

(Starting date July 2002)
Design of the QTS-2 (lab) and QTS-3 (site) systems

Incorporates reference crystal (uncoated) and test crystal where output signal is a frequency difference and gives the actual coating frequency or loading on the crystal. This will be referred to as $F (kHz)$. Use of paired crystals minimises influence of $T$.

- Measured damage is then calculated from the change in the value of $F (kHz)$ referred to as $f (Hz)$ and expressed as a ratio $(f/F)$ ie change in Hz per kHz of coating.

QuartzTec

Web site http://www.quartztec.com
Innovative tool QTS-3 based on piezoelectric quartz crystal technology

Charlottenborg Castle, Copenhagen
**PQC array data at sites** (continuous data loggers)

**Petrie, London PET**
- TWPI: 51 years
- $NO_2$: $65 \times 10^3 \, (\mu g/m^3) \, \text{hrs}$
- Light: 15.9 Kluxhrs
- 42 days (Jan)

**Charlottenborg Castle CHB**
- TWPI: 106 years
- $NO_2$: $47 \times 10^3 \, (\mu g/m^3) \, \text{hrs}$
- Light: 9.5 Kluxhrs
- 96 days (Dec-March)
Laboratory calibration of PQC arrays controlled gas flow and RH

http://www.quartztec.com

QTS-2
**WP3 Results**

*Calibration* Mastic coated crystals \((f/F)\) vs hrs

Exposed for **14hrs NO\(_2\) (10ppm) (269x10\(^3\) (ug/m\(^3\)) hrs**

Exposure 10ppm 12 hrs gives same response as 20ppm for 6 hrs
WP 3

Calibration Mastic (f/F) vs Dosage (ppm hrs)

Results

14hrs NO₂ (10 ppm) (2.69 x 10³ (ug/m³) hrs)

-f/F vs ppmhrs-

Petrie Museum 29.7 ppm hrs (1 month) \[56.4 \times 10^3(\text{ug/m}^3)\text{hrs}\]

NMD_V 11.57 ppm hrs (1 month) \[21.9 \times 10^3(\text{ug/m}^3)\text{hrs}\]
Top 2 curves unexposed crystals, lower blue curve previously exposed to NO$_2$ and the lower 3 traces from coated crystals exposed only to air. Further testing has involved exposure to NO alone (which showed no response of the resin mastic coated crystals), SO$_2$ (5ppm for 40hrs) (50%RH) which showed a smaller response than NO$_2$ ($f/F$ c 2-3)
WP5

1(a) Summary of (f/F) 1(b) integration of climate data with PQC arrays (f/F)

2. Analysis of pollutant aged coatings on PQC arrays (XPS)

3. Integration of PQC array (f/F) data with physicochemical data of coatings (accelerated and naturally aged).

4. Overall integration of steps 1&3 for enhanced damage assessment of sites

5. Protocol of damage assessment made accessible to end-users.
WP5 1a. Summary of PQC (f/F)mastic coated crystals

Summer to winter ALC (MM) NMD(134)
Main diff NO₂, NOx, HONO, HNO₃, & O₃

Winter to spring SAC and Osterley Manor (OST)
Main diff NOx
On 2nd exp increase in indoor NO₂ in OST & large increase in O₃
WP5 1a. Summary of PQC ($f/F$) mastic coated crystals (English Heritage)

Winter to spring

At Ranger’s House (RA)

Chiswick (CH)

Main diff NOx
End-users: English Heritage (Ranger’s House)

Rangers
(10.03.04-10.05.04)
f/F(RM) = 16
c.f. Chiswick
f/F(RM) = 25

Other Prospective end-users (Mexico)
Museo Nacional del Virreinato
Museo Franz Mayer
WP5 1a. Summary of PQC \((f/F)\) mastic coated crystals  

“Dosimeter Map”

Sites Introduced

Chiswick House: CHS

Ranger’s House: RA

British Library: BL

Accademia Florence: ACF

PET showcase

Days of Exposure

NMD V

ACF

PET

CHS

ACF

PET showcase

(f/F) Mastic
WP5 1b. Integration of climate data with PQC arrays
(f/F) Summer exposures 30 days

Results

Highest (f/F)

NMD_V [lowest TWPI]

next is PET
also with highest NO₂ dose.

and ALC with highest O₃ dose.

White [f/F] Blue: NO₂ [1/1000]  Dk.red: TWPI

L.green: O₃ [1/1000]
WP5  1b. Integration of climate data with PQC arrays
(f/F)  Winter exposures  30 days

Results
lowest (f/F) occurs in ALC and RA which have highest TWPI values

White (f/F)  Blue NO₂ [1/1000]  Dk.red TWPI [1/10]
L.green  O₃ [1/400]
WP5 2. Analysis of pollutant aged coatings on PQC arrays

Summary of analysis by X-ray Photoelectron Spectroscopy

- Exposure of egg tempera coated crystals to NO$_2$ causes a reduction in the surface concentration of phosphatidyl dicholine (PC). *Fatty acid components increase at the surface.*

- Exposure of resin mastic coated crystals to NO$_2$ cause an increase in carbonyl and hydroxyl functionalities in the surface of triterpenenoid mastic.

R.H.West et al., Surface and Interface Analysis (2004) 36 (8)862-865
Integration of PQC array (f/F) data with physicochemical data (FTIR) mastic on steel substrate (accelerated light aged).

Correlate changes in CO & f/F for mastic coated crystals

Site exposed show regular changes on prolonged exposure consistent with mass increase. So mastic suggested for use with crystals.
WP5  3. Integration of PQC array (f/F) data with physicochemical data of coatings (palette steel)

Blue CO (*2.5)  Red (f/F)  White [increase in loss of cis unsaturation] (*100)  L.green  klux hrs(/10^4)

British Library (f/F) mastic and chemical changes quantified in egg coated strips by FTIR
Damage categories for mastic according to $f/F$ (defined by light ageing of coated dosimeters) so that $f/F > 10$ (equiv. c. to 8 days of light ageing).

- **Cat 1** <5 (<2d (1.5 museum years))
- **Cat 2** <7.5 (<4d)
- **Cat 3** (<12 >4 &<8d)
- **Cat 4** >12 (>8d)
Conclusions re Crystal Dosimeters

1. Damage dosimeters based on mastic coated crystals provide a measure of the oxidising nature of the microclimate.

2. Increase in $f/F$ with exposure. Affected by light, NO$_2$, O$_3$.

3. Oxidative changes show as broadening of carbonyl & contribute to mass increase. Reversible small background fluctuation with variation in RH

4. Egg coated crystals also are altered by NO$_2$, light & O$_3$. Stronger response to NO$_2$ than mastic.

5. For egg tempera coated crystals increase in $f/F$ occurs in controlled environments. Unsuitable for crystal site exposure due to significant variation with RH and in some cases susceptible to loss of hydrocarbon. Suitable on strip palettes.
Overview of main project results

1. **Reduction of the climate data** has allowed the description of the sites in terms of their **potential for damage** (National Museum of Denmark).

2. Creation of software, **Grand Unified MIMIC Database “GUMD”**, to organise climate data (National Museum of Denmark).

3. **Dosimeter calibration** achieved by exposure to accelerated light and pollutant dosages (NO₂ at selected RH, preliminary studies on effect of HNO₃).

4. **FTIR database for coatings (strips on palette)** (BbK). **DTMS database for paint** (FOM Institute).

5. Correlation of chemical changes with measured crystal frequency shifts.

6. **Ranking of sites in terms of monitored damage**.
EC 5th Framework DGXII “Protection & Conservation of European Cultural Heritage” for funding the MIMIC project
Nancy Wade, paintings conservator
University of London, Birkbeck College, Dr. J. Slater, Dr. M. Appleton (QuartzTec)
Dr. C. Theodorakopoulos, Dr. Q. Wang, R. Campana, Dr. A. Beard, and C. F. Wilson
University College, Dr. K. Pratt (UCL Chem)
CNR- Istituto Inquinamento Atmosferico & IROE-CNR,
Dr. F. de Santis, Dr. M. Bacci, Dr. M. Picollo, CNR-Rome and Florence, Italy
El Alcázar, Segovia, Spain, Victoria Smith.
National Trust, U.K., Linda Bullock,
National Museum of Denmark, Copenhagen, Morten Ryhlov-Svendsen, Dr. Tim Padfield, and Lars Aasbjerg Jensen
FOM Institute (Netherlands) Prof. J. J. Boon & Dr. E. Ferraira
Tate Britain Conservation Dept., Dr. B. Ormsby, Stephen Hackney & Dr. J. H. Townsend
Winnats Scientific Services Dr. R. West, XPS analysis
English Heritage David Thickett
British Library K. Matsuoka