Dosimeters for indoor microclimate monitoring for cultural heritage

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Abstract

This paper describes the performance of dosimeters based on the quartz crystal microbalance and demonstrates that measured changes can be correlated with damage to artifacts and with environmental conditions. The work has been performed in the framework of two EC projects where the emphasis has been on damage assessment. In the MIMIC project: [Microclimate Indoor Monitoring for Cultural Heritage Preservation] [EVKV-CT-2000-00040], piezoelectric quartz crystals (PQC) were covered with organic coating. It was the damage to these coatings which was assessed after exposure to a range of environments [1]. The eight-crystal arrays were accommodated in custom built modules and exposed either as passive samplers or as continuous monitoring devices, which recorded weight changes in real time. The Artists' materials, resin mastic varnish and egg tempera, were selected, since mass spectrometric studies had shown that there was a correlation between chemical change and exposure to light [2, 3]. Accelerated light ageing tests of the coated crystals then demonstrated that changes were correlated with changes to the oscillation frequencies of the coated crystals. Furthermore, real time monitoring of exposure to controlled and varied levels of NO_2 and RH provided evidence of a systematic variation in the frequency shifts of the coated crystal arrays [1]. Crystal arrays were also exposed in rooms containing mixed collections in museums, historic houses, and castles, where climate and pollutants, were being monitored [1]. The results obtained from the integration of climate, dosimeter, and chemical data will be discussed in this paper. In the SENSORGAN project (contract no. 022695: Sensor System for Detection of Harmful Environments for Pipe Organs) a lead coating was used. Lead was selected as it was shown in the COLLAPSE project (Corrosion of lead and lead-tin Alloys of Organ Pipes in Europe) [4] that lead was the main constituent of historic organ pipes and that damage occurred as a result of the emission of volatile organic acids from the wood of the wind-chest. Modules containing crystal arrays were exposed to accelerated ageing in laboratory cabinets where levels of acetic acid were monitored. Site monitoring was performed in the organs in two churches: (1) the Minor Basilica of St. Andrew the Apostle (1611) in Olkusz, Poland (2) St. Botolph without Aldgate (1704) London, England.

Introduction

This paper describes the use of dosimeters to assess cumulative damage to indoor cultural heritage due to the environment. In the MIMIC project, organic coated piezoelectric quartz crystals were made and their performance in museums and historic buildings was evaluated [1]. The principle of operation of the PQC crystals is that their oscillation frequency depends on the mass of the coating, as related by the Sauerbrey equation [1]. The piezoelectric quartz crystals (PQC) were coated with either resin mastic artists' varnish or egg tempera medium. These coatings were selected since previous mass spectrometric (MS) studies had shown that the degree of oxygenation of the egg lipid components in egg tempera was directly related to the duration of light exposure [2]. MS studies of resin mastic also showed that ageing results in addition of oxygen to the resin compounds, as well as the simultaneous loss of hydrogen [3]. Furthermore, MS studies demonstrated that controlled accelerated light-induced deterioration of mastic coatings on PQC crystals was accompanied by systematic changes in the crystal frequency [5].

Within the framework of the MIMIC project, custom built modules were developed to house arrays of eight coated PQC crystals, which were connected to electronic circuitry for data reduction and storage [1]. This paper presents the results obtained from the integration of climate, dosimeter, and chemical data at various test sites. To facilitate comparison with the dosimeter output, indoor relative humidity (RH) and temperature (T) data were reduced to Time Weighted Preservation Index (TWPI) values [6], and light levels were expressed in accumulated dose, expressed as (klux hours). Pollutant levels of NO_2, NO_x, HONO, HNO_3, O_3 and SO_2 were also expressed in terms of received dosage, in $\mu g/m^3 \times$ hours. The environmental and the dosimeter output data are summarised on the website of the MIMIC project (http://iaq.dk/mimic) and are available on request [1].

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One of the objectives of the current SENSORGAN project is to adapt this piezoelectric based dosimeter to detect the presence of organic acids, which are corrosive to organ pipes [1]. Lead is deposited on the PQC crystals by thermal evaporation. The reason for choosing lead is to provide a coating which will mimic the damage that occurs in lead based organ pipes. Volatile organic acids, predominantly acetic acid, which are generated in the windchest, typically made of oak or pine wood, corrode the lead pipes. In the COLLAPSE project, heavily corroded pipes of 96% lead content were observed in the St Jakobi church (Lubeck, Germany) [4]. The starting point of the SENSORGAN project was to use only lead coating for the PQC crystals, together with lead coupons. The latter are routinely used to monitor display cases in museums. Information on the dosage level [1]of acetic acid which causes damage have been published [7].

Experimental

Crystal arrays (8) were mounted in prepared modules as described elsewhere [1]. Accelerated light ageing at 18,000 lux was performed by exposing modules for periods of 1-16 days [1]. Real time monitoring of the response of egg and resin mastic coated PQC crystals to NO_2 was performed by [1] subjecting them to controlled flows and levels of NO_2 at selected values of RH at ambient temperature. Crystals were also exposed at test sites [1] where environmental conditions (RH, T, pollutants NO_2, NOx, HONO, HNO_3, O_3, SO_2, light) were recorded [1].

Accelerated ageing was then performed by exposing modules of PQC arrays in cabinets containing blocks of oak and pine wood at 65% RH for extended periods. Levels of acetic acid were monitored using A-D strips [8]. Crystals were also exposed in an old showcase in Kenwood House where levels of acetic and formic acid had been measured by diffusive passive samplers. Test sites included St. Botolph without Aldgate (London) where restoration work had just been completed and the church of St Andrew the Apostle, Olkusz, Poland.

Results of the MIMIC project

Summary of selected climate data and dosimeter values

Table 1 shows the dates and duration of exposure of the mastic coated PQC arrays in the Petrie Egyptology Museum (PET) (London) together with the dosimeter output expressed as *[Δf(*Hz*)/F(*kHz*)]*, which is the ratio of the frequency shift to the original coating frequency *[F*(kHz)*]*. Values of this ratio at PET are significantly higher than those obtained on exposure in the selected Reading room in the British Library (BL, Table 2). The environment in BL is air conditioned in contrast to PET, where there is no climate control. Both sites are in a similar location in central London. However, measured indoor concentrations of NO_2 differ; PET has values typically 40-60μg/m^3 and BL 10-20μg/m^3. The climate data in Table 3 includes these sites and shows that NO_2 dosage levels were higher at PET and probably caused the higher level of dosimeter damage. This is supported by accelerated ageing studies that have shown that NO_2 contributes to the degradation of mastic [1].

Petrie Museum	Dates		Days	PQC mastic
PET	Start	End		Δf (Hz)/ F(kHz)
Exposure 1	2.7.02	12.7.02	10	6.8
Exposure 2	12.7.02	16.7.02	14	10.1
Exposure 3	16.7.02	2.8.02	31	15.3
Exposure 4	2.8.02	7.8.02	36	18
Exposure 5	7.8.02	16.8.02	45	19
Exposure 6	16.8.02	21.8.02	50	18.9
Exposure 7	21.8.02	29.8.02	58	22.1
Exposure 8	29.8.02	11.09.02	71	23.8
Exposure 9	12.9.02	18.09.02	77	22.2
Exposure 10	18.9.02	27.09.02	86	24.4
Exposure 11	27.9.02	09.10.02	99	26.6
Exposure 12	09.10.02	14.10.02	104	30.5

Table 1. dates and duration of exposure of the resin mastic coated PQC arrays in the Petrie Egyptology Museum (PET), London, together with the dosimeter output values.

British Library				
BL	Dates		Days	PQC mastic
	Start	End		Δf (Hz)/ F(kHz)
Exposure 1	17.02.04	23.03.04	35	3.3
Exposure 2	01.04.04	06.05.04	70	7.1
Exposure 3	04.06.04	28.07.04	124	8.1
Exposure 4	30.07.04	06.09.04	162	9.2
Exposure 5	08.09.04	05.10.04	189	8.8

Table 2. dates and duration of exposure of the resin mastic coated PQC arrays in the British Library (BL), London, together with the dosimeter output values.

Table 3 lists values for selected climate data with dosimeter output values for urban non-conditioned sites, including PET, National Museum of Denmark (NMD_V, NMD_134), Charlottenborg Palace, Copenhagen (CH), Chiswick House, London (CHS), as well as semi-rural non-conditioned sites, including the Alcazar (castle) in Segovia, Spain (ALCMM and ALCC). The dosimeter values together with Time

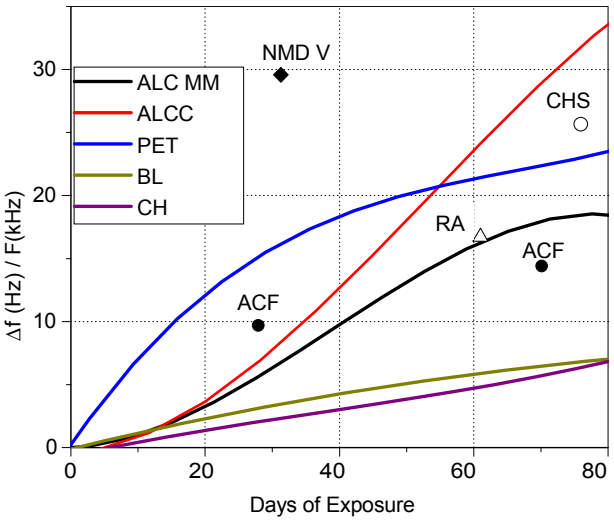

Figure 1. The results from prolonged site exposure of PQC modules were summarised by plotting the dosimeter output values against days of exposure. The data were fitted using regression analysis to provide a "dosimeter map" of the sites monitored [1].

Weighted Preservation Indices (TWPI) [8], light, and pollutant dosages (NO_2 ,O_3) are shown. These data represent approximately 30-day exposures. It is observed that the highest dosimeter values and highest coating damage [1]occur at sites where levels of light (NMD_V) and levels of NO_2 (PET) are highest. Lowest dosimeter output values occur for low NO_2 levels at BL and CH where, in addition, the TWPI value is high (indicating both low temperature and low RH) [6]. In the case of ALCMM and ALCC the higher values for O_3 probably contribute to the high value of the dosimeter readings. Between the two latter sites, ALCC has higher levels of light that is reflected in the dosimeter readings [1].

Graphical summary of readings from dosimeters exposed at selected test sites

The results from prolonged site exposure of PQC modules were summarised by plotting the dosimeter output value against days of exposure. The data were fitted using regression analysis to provide a "dosimeter map" of the sites monitored (Figure 1). Point values correspond to exposures in NMD_V (entrance hall),

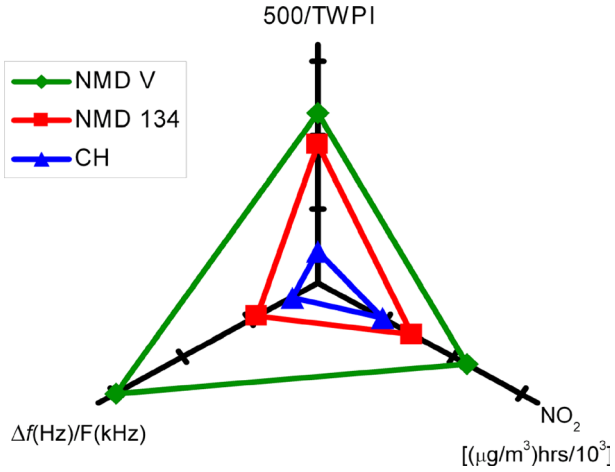

Figure 2. Shows a plot for the calculated Time Weighted Preservation Indices (TWPI), values of NO2 dosage and dosimeter output values for the 3 sites in Copenhagen in the National Museum of Denmark (entrance hall NMD_V, and room 134 NMD_134), and Charlottenborg Palace, Copenhagen (CH) [1].

1st and 2nd exposures near the statue of David (ACF) (Galleria dell'Accedemia, Florence, Italy), as well as in Chiswick House (CHS) and Ranger's House (RA) (English Heritage, London). It is clearly demonstrated that where conditions are uncontrolled then the damage values are similar to those observed in the Petrie Museum (PET). The air-conditioned site BL showed minimum damage and the non-conditioned site NMD_V showed maximum damage. The similar damage levels shown for CH and BL, may be due to the high TWPI value of CH. Figure 2 shows a plot for the TWPI, NO_2 dosage, and dosimeter output for the 3 sites in Copenhagen (NMD_V, NMD_134 and CH). For CH the high TWPI value (indication of a good quality environment) and lower NO_2 dosage levels than NMD_V gives rise to a lower dosimeter output.[2].

Results from the controlled light ageing measurements relate dosimeter values to duration of exposure. Values greater than 15 [2] were found to be equivalent to 16 days light ageing, less than 15 but greater than 8 were equivalent to 8 days light ageing , and greater than 4 but less than 8 were equivalent to 4 days light ageing. In addition, we calibrated

Start	End	Site	*Δf (Hz)/F(kHz)*	TWPI	Light	O_3	NO_2
03.07.02	12.08.02	NMD_V	29.5	22	4304	12.2	21.9
16.07.02	02.08.02	PET	15.3	47	1.3	2.2	56.4
03.05.03	06.06.03	ALMM	9.6	52	33.5	15.6	4.7
03.05.03	06.06.03	ALCC	10.3	54	82.4	15.7	5.5
20.12.02	21.01.03	CH	3.6	116	2.9	1.1	9.4
03.06.02	03.07.02	NMD_134	9.0	27	17.3	3.4	13.9
03.11.03	05.12.03	CHS	7.3	61	62.4	4.7	31.1
17.02.04	23.03.04	BL	3.3	39	33.6	1.6	9.5

Table 3. values of selected climate data; calculated values of TWPI (years), received dosages of light (kluxhours) and pollutants NO_2 and O_3 [(μg/m$_3$)×hours×103], and dosimeter output values for exposure periods shown.

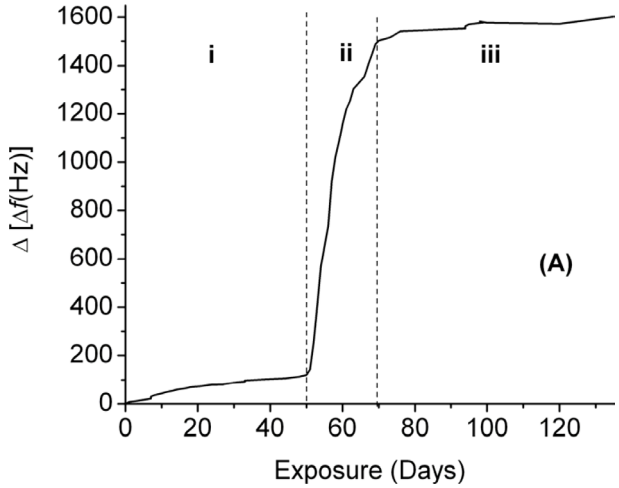

Figure 3. Values are shown for the frequency shifts [Δf (Hz)] vs duration of exposure for lead coated PQC crystals in cabinets containing oak and pine blocks and the subsequent changes with higher RH [1].

the response of mastic coated PQC crystals using NO_2 in the dark. Exposure to 10 ppm NO_2 for 14 hrs gave dosimeter output values of about 8. FTIR spectroscopy of coated crystals exposed to various levels of NO_2 showed broadening of the carbonyl absorbance bands. These changes were evaluated at the molecular level by X-ray photoelectron spectroscopy [9]. Overall, four categories of damage classification were defined. Values for dosimeter output according to chemical damage have been allocated as follows: class 4 >15, class 3 > 8, class 2 > 4 , and class 1 <4 [2].

Correlation of PQC data, climate, and chemical data (FTIR) together with the effect of accelerated ageing (light and pollutant), to assist damage estimation

The mastic coated PQC crystals showed maximum damage (class 4) in the case of NMD_V (Table 3). FTIR spectra of both mastic and egg tempera samples, from similarly exposed coated strips, showed significant chemical change. The egg tempera samples lost cis-unsaturation completely, whereas there was extreme broadening of the carbonyl peak in mastic. In the ERA (Environmental Research for Art Conservation) project [10] it was observed by FTIR that unpigmented films (egg only tempera) had a greater response to pollutant ageing than to light ageing. Hydrolysis, leading to the formation of free fatty acids, is more extreme with pollutant exposure (NOx and SO_2) than light exposure. This was also observed by direct temperature resolved mass spectrometry (DTMS) [11] [2].

Results from the SENSORGAN project

Preparation of lead coated crystals and accelerated ageing

Lead coatings were applied to piezoelectric quartz crystals using a thermal evaporator specifically designated for the deposition of low vapour pressure metals [12] [2].The changes that were observed after deposition are summarised in Table 4 [2]. The dosimeter output as for the organic coatings is calculated as described above. In the case of the lead coatings where the formula weight is well defined it is possible to calculate the mass gain and extent of oxidation of the lead metal [2]. For example in Table 4, an initial lead loading of 12,857 Hz (F_0) corresponds to a mass of 8.99 μg [2]. Changes after selected periods of 5-60 days are shown and the change in mass is calculated. Continuous monitoring was performed on canned crystals, where the surface is protected from direct exposure. The PQC crystals were then used uncanned for accelerated ageing and exposure at sites [2].

Humid acidic environments were generated by placing wooden blocks of oak and pine into two cabinets [2]. The increase in acetic acid emission from the oak block and was monitored by the colour change in A-D strips [8]. Acetic acid was readily detected, which indicated that levels were at least (2500 μg/m^3) [13]. Weight increases in lead coupons exposed in the oak containing cabinet were also monitored, and gave values similar to those obtained in the COLLAPSE

PQC lead						
Duration (days)	0	t=5	t=10	t=15	t=30	t=60
F initial frequency (Hz)	12857					
Ft frequency (Hz) at t		13018	13079	13123	13219	13304
Δf (Hz)	0	161	222	266	362	447
[Δf (Hz)/F(kHz)]	0	12.5	17.3	20.7	28.2	34.8
Mass	Mo (initial)			Mt post-deposition		
Mass (μg) at t	8.99	9.11	9.16	9.19	9.25	9.31
Δm Mass gain (μg)	0	0.12	0.17	0.20	0.26	0.32

Table 4. The changes in dosimeter output values are shown together with mass gain (%) of lead coated PQC crystals after selected periods (5-60 days) of continuous monitoring.

project [14]. The lead coupons exposed in the cabinet with the pine block had a lower mass gain due to the significantly lower emission rate of acetic acid [15]. Consequently the exposed lead coupons showed that the atmosphere generated by oak is more aggressive than that of pine. This supports previous observations on differences on exposure of lead to oak and pine [15] [2]. The RH influences the response of lead in both environments: as RH increases so does the mass gain.

The response of lead coated crystals to the environment in the oak cabinet initially at low RH (30-40%RH) showed a frequency shift of the order of 200-300Hz over several days. When the RH was increased to 50% and then to 65% there was a progressive shift in the rate of change of frequency. In Figure 3 values of the frequency are plotted against time (days). Two sets of crystals are shown: one pair was placed in the oak cabinet on Sept 9th 2006 and the other a month later. This accounts for the initial frequency differences as the first pair had already been exposed to the oak block for one month. From the end of November 2006 the RH in the cabinet was increased. The higher RH promoted in both cases an increase in the rate of frequency shift. Crystal (B5_3) which was inserted in the oak cabinet at RH (65%) showed a change of 1500 Hz over 1-2 days. In terms of the dosimeter output, the value is 110, which exceeds the values observed for changes reported in organic based coatings in the MIMIC project. Two pairs of crystals that had been previously exposed to acetic acid (i.e already tarnished) showed a smaller increase in frequency with increase in RH than those inserted into the cabinet at the later time when the RH had increased. It has been previously observed that RH changes have a greater influence on weight gain of untarnished compared with tarnished lead samples [16][2].

Crystals exposed in the pine cabinet showed a frequency shift of the order of 130 Hz, which was 30% lower than that exposed in the oak cabinet. This difference in behaviour has been previously reported for lead coupons [15]. When the RH in the cabinet was increased to 65%, a further shift of 800Hz occurred. The response in the oak cabinet for a similar period was 1500 Hz. Figure 3 demonstrates the difference in lead coated crystal response between the oak and pine containing cabinets and the subsequent increase with higher RH [2].

Selected coated crystals were placed in the modules and sent for site exposure, in some cases together with lead coupons. The crystal modules allowed free diffusion of air but were protected from physical damage by a wire gauze screen. Exposure of lead coated crystals in PQC passive sample holders [2] took place initially at Kenwood House, and St. Botolph without Aldgate, both buildings in London. At Kenwood the dosimeters were placed in a showcase where levels of acetic and formic acids had been previously measured [acetic acid 3847±80 μg/m3, and formic acid 1262±38 μg/m3]. Exposure at this concentration in an enclosed space for periods of several months has been shown to cause damage to lead objects [7]. This allowed correlation of frequency and/ mass change with significant damage. At St. Botolph without Aldgate the PQC array was placed within the wind chest of the organ, together with lead coupons.

The rate of change [2] in the lead coated crystals in the showcase at Kenwood for a period of one month was similar to that obtained on exposure to 650 ppb acetic acid at 74% RH for 10-12 hours. The dosimeter value was between 100-165. Exposure in the wind chest of the organ at St Botolph gave a slightly lower dosimeter output value between 80-130. In comparison the crystal array placed in the historical organ in Olkusz gave lower values between 14-30.

Conclusions

Resin mastic PQC crystals have provided dosimeters that are sensitive to light and oxidising agents (NO_2, ozone), which show a differential response at sites where these conditions vary. Lead coated crystals have provided dosimeters which respond to organic acids (e.g acetic and formic acids). They also show a differential response on exposure to environments where there are different levels of acetic acid. Preliminary site tests indicate that the environment in the organ in St. Botolph shows a high level of change in the crystal array, and there are indications that emissions from the new wood (mainly pine) used in the wind chest are contributing to the damage shown by the lead coupons [2]. In future, both coatings will be used in crystal arrays for monitoring cultural objects in microclimate frames (EC project PROPAINT Improved protection of Paintings during exhibition,storage and transit).

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