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Original article

Pollution monitoring by dosimetry and passive diffusion sampling for evaluation of environmental conditions for paintings in microclimate frames

Terje Grøntoft[a,*], Marianne Odlyha[b], Peter Mottner[c], Elin Dahlin[a], Susana Lopez-Aparicio[a], Slawomir Jakiela[b], Mikkel Scharff[d], Guillermo Andrade[e], Michal Obarzanowski[f], Morten Ryhl-Svendsen[g], David Thickett[h], Stephen Hackney[i], Jørgen Wadum[j]

[a] Norwegian Institute for Air Research (NILU), P.O.box 100, NO-2027 Kjeller, Norway
[b] Birkbeck College, Malet St. Bloomsbury, London WC1E 7HX, UK
[c] Fraunhofer Institute for Silicate Research (ISC), Bronnbach Branch, D-97877 Wertheim, Germany
[d] Danish School of Conservation, Royal Danish Academy of Fine Arts (RDAFA.SC), Esplanaden 34, DK 1263 Copenhagen K, Denmark
[e] SIT Transportes Internacionales S.A., Avda. Fuentemar, 13, 28820 Coslada, Madrid, Spain
[f] National Museum in Kraków, ul. Krupnicza 26, 31-123 Kraków, Poland
[g] Nationalmuseets bevaringsafdeling, IC Modewegsvej, Brede, DK-2800 Kgs. Lyngby, Denmark
[h] English Heritage, 1, Waterhouse Square, 138 Holborn, London EC1N 2ST, UK
[i] Tate Britain, Millbank, London SWIP, 4RG, UK
[j] Statens Museum for Kunst (SMK), Sølvgade 48-50, DK-1307 Copenhagen K, Denmark

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ABSTRACT

Pollutants and their potential degradation of paintings have been measured for the first time in microclimate frames (mc-frames), which are used to protect paintings. The pollutants that were measured include both inorganic pollutants, which originate mainly from external sources, and organic pollutants from mainly internal sources. Those originating from the outdoors enter rooms and subsequently mc-frames at a rate depending on the ventilation rates (air exchange rates) of the mc-frames. The concentration of gaseous pollutants emitted within the mc-frames will depend on net emission rates of the materials used to make the mc-frames, their design, and their ventilation rates. In the EU PROPAINT project measurements of gaseous air pollutants and climatic conditions were performed at various locations both inside and outside different state-of-the-art mc-frames. Diffusive passive pollution gas samplers were used together with different types of dosimeters. Results show that the dosimeters respond to either the photo-oxidizing conditions or the level of volatile organic acids in the environments both in the museums and within the mc-frames. Two dosimeters, the Early Warning Organic (EWO) made from a synthetic polymer and the Resin Mastic coated Piezo electric Quartz Crystals (RM-PQC) respond to photo-oxidation and showed higher values outside than inside the mc-frames. Two other dosimeters, the Glass Slide Dosimeter (GSD) and the Lead coated Piezo electric Quartz Crystals (L-PQC) respond to volatile organic acids and yielded higher values inside than outside the mc-frames. This study emphasizes the need for further work to determine environmental damage functions for paintings, in particular for the effects of organic acids. Such information is essential for the evaluation of the protective effects of mc-frames for paintings. The use of mc-frames is increasing and it is very important to know that this protective measure does not introduce new risks.

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1. Research aims

A major aim of the EU project PROPAINT (FP6 SSPI Nº 44254) (2007–2010) [1] was to evaluate the protective effect of microclimate frames (mc-frames) for paintings against gaseous air pollutants by the combined use of novel dosimetry technology developed in previous EU projects. Concentrations of single pollutant gases, temperature and RH were measured to determine the sensitivities of the dosimeters and to produce environmental dose-response equations. Research was performed to establish the

* Corresponding author. Tel.: +47 63 89 80 00. fax: +47 63 89 80 50.
E-mail addresses: teg@nilu.no (T. Grøntoft), m.odlyha@bbk.ac.uk (M. Odlyha), mottner@isc.fraunhofer.de (P. Mottner), emd@nilu.no (E. Dahlin), sla@nilu.no (S. Lopez-Aparicio), ms@kons.dk (M. Scharff), artyd.info@gmail.com (G. Andrade), mobarzanowski@muzeum.krakow.pl (M. Obarzanowski), Morten.Ryhl-Svendsen@natmus.dk (M. Ryhl-Svendsen), David.Thickett@english-heritage.org.uk (D. Thickett), Stephen.Hackney@tate.org.uk (S. Hackney), j.wadum@smk.dk (J. Wadum).
URL: http://www.nilu.no/ (E. Dahlin).

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dosimeter technology and methodology for simple assessment of the environmental degradation risk for paintings inside mc-frames. The results from the dosimeter measurements were compared with evaluations of tolerable environmental doses (pollutant gases, temperature and relative humidity [RH]) for museum objects and presented in a readily accessible form for potential users.

2. Introduction

The use of mc-frames for paintings during exhibition, storage, and transport has become common in many European museums. Mc-frames are used to protect paintings against physical damage, externally generated pollutants, vandalism [2], and in some cases they offer microclimate buffering [3]. A potential negative effect is that mc-frames trap possible internal emissions of Volatile Organic Compounds (VOCs) including formic and acetic acid [4–6], that they can function as "green houses" and be favourable for microbiological [2] and insect species [7]. This paper discusses the use of dosimetry to assess environmental conditions in mc-frames used for the preservation of paintings and is based on results obtained in the EU PROPAINT project. Diffusive passive pollution samplers usually measure, or are analysed to detect, single pollutant gases. Dosimeters can measure the generic effect of the total, or parts of the total, environment comparable to that on cultural heritage objects of interest, outdoors or indoors. This is useful because measurement of some or all single concentration of pollutants or values for climate parameters do not directly inform about the degradation effects on objects. Climate and air pollution accelerate together in a synergistic way the degradation of materials.

The purpose of dosimetry is to measure this effect in a more direct way. For a dosimeter to be useful it must be possible to correlate the effects on the dosimeter with those on objects and also the dosimeter must be more sensitive than the art works. This can be achieved by the use of a dosimeter material similar to that used in the objects themselves. Alternatively, the relationship between the reactivity of the dosimeter and that of the art works can be found by correlating the impact on both with the same degrading environmental parameters, such as pollutant gases, temperature and RH. Then relatively rapid dosimeter measurements of the degradation risk can be made.

A painting usually consists of many different materials that react differently with the environment, and the degradation of a painting will therefore depend on the susceptibility and interaction of the materials employed by the artist [8,9]. Moreover, later conservation treatments may influence the reactivity of an object to external pollutants, and may even add additional emissions to the internal environment of a mc-frame. Thus, many different dosimeters may potentially be needed to evaluate the overall environmental risk to objects. A simpler alternative is to decide on the generally acceptable levels for measured effects on a dosimeter that are valid for separate collections of particular kinds of objects having similar environmental sensitivity. These can be collections of e.g. paintings, archival materials, metals or wooden objects. The dosimeters used in PROPAINT were sensitive either to photo-oxidative degradation processes or to attack by volatile organic acids, and are suitable for risk assessment for both organic-based and inorganic materials.

3. Methodology

3.1. Dosimeter measurements, sampling locations and periods, and statistical analysis

Four different dosimeters were applied (Fig. 1): The Early Warning Organic (EWO) dosimeter developed by the Norwegian Institute for Air Research (NILU, Norway) in the EU project MASTER (EVK4-CT-2002-00093), the Resin Mastic (RM-PQC) and Lead coated Piezoelectric Quartz Crystal (L-PQC) dosimeters developed at Birkbeck College (United Kingdom) in the EU projects MIMIC (EVKV-CT-2000-00040) and SENSORGAN (Contract no. 022695), respectively, and the Glass Slide Dosimeter (GSD) developed by the Fraunhofer Institute for Silicate Research (ISC, Germany) in the EU project AMECP (EV5V-CT-92-0144). In addition, lead coupons were exposed with the L-PQCs. The technical specifications, measurement methodology, previously found environmental sensitivity and determined impact levels for cultural heritage objects for all the dosimeters are reported in [10–17]. For the weighing of the lead coupons, of size 20 mm × 10 mm and weight 500 mg ± 0.01 mg, a Sartorius (4401 MP8) electronic microbalance with a sensitivity of 0.1 μg was used. – Basically the impact levels were determined by comparing observed and reported impact by single environmental parameters on cultural heritage objects [18] with those on the dosimeters (Table 2). Inside the mc-frames where size restricted the use of arrays of eight PQC-dosimeter crystals (four RM-PQC and four L-PQC) then two to four crystals clamped between steel plates were suspended within the mc-frames. The difference in the frequency shift for the PQCs was measured before and after the exposures. The frequency shifts were much higher for the L-PQC than for the RM-PQCs and were calculated as the percentage change in frequency. L-PQC values are only compared between themselves, as are RM-PQC values, and the different units can be compared to results in [14–17]. A new miniaturised prototype for measuring in real time of frequency change in the crystals has been recently developed for use within the restricted environment of the mc-frames. The GSDs have for the last 15 years been applied widely as environmental impact sensors for cultural heritage, indoors in museums, in showcases, and outdoors. For the PROPAINT exposures reported in this work the GSD version M1.0 with fire polishing finish was used.

All the dosimeters (PQC, EWO and GSD) were exposed simultaneously for three months (2007/08) inside and immediately outside mc-frames for paintings. The mc-frames were either with or without paintings. They were installed in different locations, which included workshops, storage areas and locations in galleries. Nine sites (13 locations), eight in Europe and one in Mexico, were used (Table 1). Two general types of mc-frame designs were tested: "Modern" new mc-frames purpose built by the SIT-Artyd Company and "historical" mc-frames adapted to existing picture frames (Fig. 1 and Table 1). All sites except four (No. 1, 5, 6 and 7, Table 1) had paintings installed in the mc-frames. The SIT-Artyd mc-frame (No. 1, Table 1) was arranged as a "worst case scenario" and a fresh oak panel prepared with a natural varnish and a polyvinyl chloride (PVC) containing old white carpenter's glue was installed.

Additional standard passive sampling of pollutant gases was performed simultaneously inside and outside the mc-frames in two periods following the dosimeter exposures: VOCs were sampled with Tenax tubes over one week. Then NO_2, O_3, SO_2, acetic and formic acid were sampled over one month with separate IVL type samplers [19]. In addition formaldehyde was sampled with SKC UME × 100 passive samplers. For the NO_2, O_3 and acetic acid results that are reported or used in this work the detection limit has been found to be 0.5 $\mu g/m^3$. For the formaldehyde sampler the detection limit is reported to be 6 $\mu g/m^3$. The air exchange rates (ventilation rates) of the mc-frames were determined in individual single experiments from the decay of the concentration of CO_2 initially injected as a tracer gas [20]. The temperature and relative humidity (T and RH), was recorded during the dosimeter exposures by the standard electronic equipment available to the conservator at each location. Statistical software SPSS+ was used to perform multiple regression analysis to determine the dependence of the dosimeter responses on the environmental parameters. The statistical sample size included values of all the measurements in the museum rooms and inside the mc-frames for all the locations (shown in

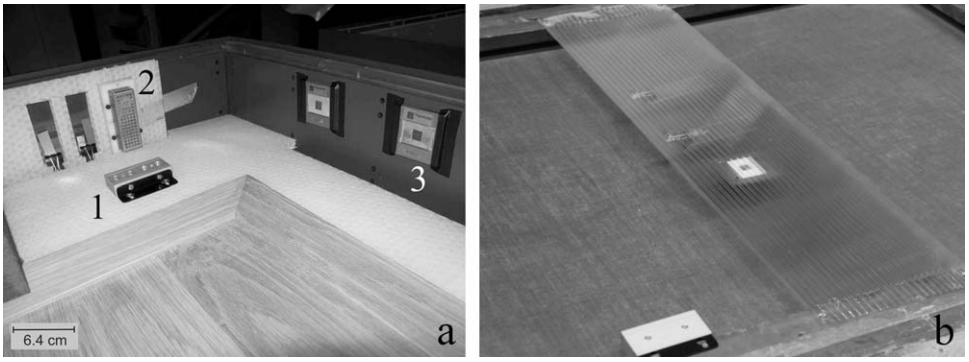

Fig. 1. Three dosimeters: 1. Early Warning Organic (EWO) dosimeter. 2. Resin Mastic (RM-PQC) and Lead Piezoelectric Quartz Crystal (L-PQC) and 3. The Glass Slide Dosimeter (GSD), mounted inside the "modern" SIT-Artyd mc-frame (a) and a "historic" frame adapted to mc-frame at The National Gallery, Oslo (b).

Table 1), except the SMK2 mc-frame for which not all measurements were performed. Some obvious outliers from the regression fit were removed from the analysis (The lead coupons in the constructed worst case frame no 1 and one of two EWO parallels at location no. 11, GNM [Fig. 2]).

3.2. Discussion of reported / recommended levels

The determination of threshold levels for pollutants in mc-frames should be based on observed degradation effects on objects themselves. However there is little information available about

Table 1
The locations for exposures in PROPAINT.

Locations	Mc-frame characteristics			
	Type of mc-frame[a]	Ventilation rate (day^{-1}) Net V(m^3)	Age. Major materials[b]	Location[b] AC = Air conditioned N = Naturally ventilated
1. SIT-Artyd workshop, Madrid, Spain	M	0.19 0.077	New 2007. Synthetic polymers, methacrylate, polycarbonate. Stainless steel. Acrylic paint, Chloroform bonding. Aluminium	Workshop (AC) Pollutants from materials, and adjacent rooms
2. NG. National Gallery, Oslo, Norway	H	0.67 0.013	30–40 years. Wood. Polycarbonate. Al tape	Public gallery (N) Painted wallboard. Cork
3. EH.A.H. English Heritage, Apsley House, London, UK	H	0.17 **(–)**	Refitted 2007. Al-foil covered wood	Public gallery (AC) Chemically filtered. Stone building. Silk. Plaster. Carpet. Brick. Wood
4. EH.K. English Heritage, Kenwood, London, UK	H	1.4 0.041	1980s. Al-foil covered wood	Public gallery (N) Plaster. Wood
5. Tate B. Tate Britain, London, UK	H	8.6 0.010	100 years. Soft wood. Oil tempered hardwood. Gesso. Gilding	Unconditioned stairwell (N) Well-ventilated. Central London Paint. Plaster. Brick. Wood. Old building
6. Tate S. Tate Store, London, UK	H	6.7 0.027	1990s. Softwood. Oil tempered hardwood Gesso. Gilding. Melinex (polyester) sheet. Gummed brown kraft paper	Conditioned storeroom (AC) Central London. Cement. Paint, Vinyl. Wood. Other frames
7. SMK1. "Statens Museum for Kunst" 1, Copenhagen, Denmark	H	(–) **(–)**	18th or 19th Century. Mc-frame in 2007. Acryl. painted balsa. Polycarb. Felt. Cork. Al-tape	Public gallery (AC) Painted gypsum walls. Lacquered wood
8. SMK2. "Statens Museum for Kunst" 2, Copenhagen, Denmark	H	0.39 0.024	(–)	In transit with painting, later empty in museum workshop
9. MBV. Fine Art Museum, Valencia, Spain	M	0.15 0.029	2005. Synthetic polymers, methacrylate, polycarbonate, neoprene. Volera-, silicon-, Al-tape. Artsorb	Public gallery (AC) Bricks. Plaster. Stone. Steel. Painted MDF
10. MNA. National Museum of Art, Mexico City, Mexico	M	(–) **(-)**	New (2007) SIT-Artyd mc-frame. Synthetic polymers	Public gallery (AC) Wood. Plaster
11. GNM. Germanic National Museum, Nurnberg, Germany	H	(–) 0.047	6 years old. Lacquer covered Al. Rubber sealing	Public gallery (N) Stone
12. NMK1. National Museum in Krakow (Leonardo frame), Poland	O	15 0.32	5 years old. Fibreboard covered with tapestry	Public gallery (N) Waxed wood. Tapestry. Lime plaster and emulsion paint. Glass ~ 60% of this enclosure
13. NMK2. National Museum in Krakow (new mc-frame), Poland	H	0.42 0.060	2007. Polycarbonate. Al profiles and foil	Public gallery (N) Lacquered wood. Acrylic painted lime plaster. Gypsum boards

[a] M = "Modern" new built. H = "Historic" modified. O = Open mc-enclosure.
[b] Glass in mc-frames and rooms is not included. (–) = not available.

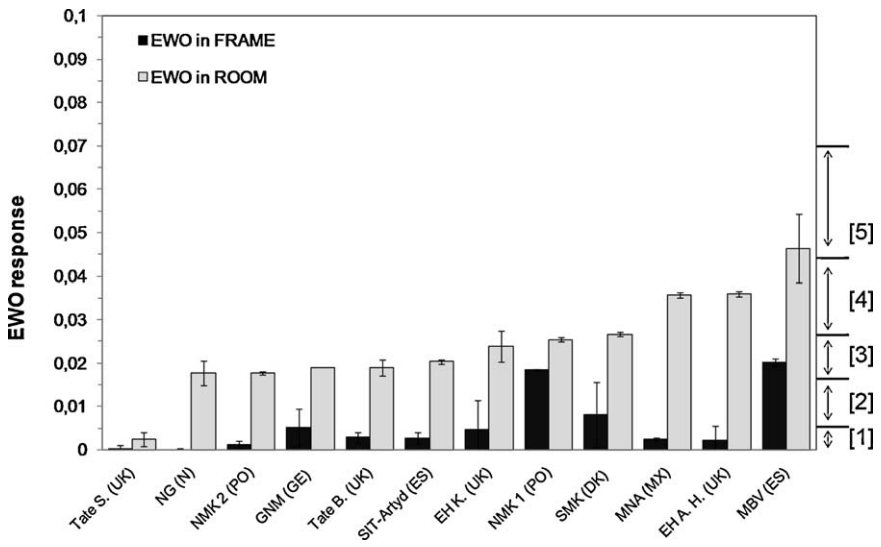

Fig. 2. Results from Early Warning Organic (EWO) (average of two parallel exposures, except in GNM room, absorption units at 340 nm). SMK = SMK1. Number in brackets are tolerability location levels [11] (at relative humidity H = 55%): [1]: Archive store, [2]: purpose built Museum Gallery, [3]: Historic House Museum, [4]: Open display in open museum, [5]: Outside store with no control.

damage impact of gaseous pollutants on paintings. Very low doses of NO_2 and / or O_3 inside a mc-frame may be equally degrading to sensitive materials / objects as a much higher concentration of acetic acid [18]. However, there is considerable difference in the effects of pollutants on different materials [18,21]. Suggested threshold levels for NO_2 and O_3 on museum objects are usually in the lower end of the range from 0 to 20 $\mu g/m^3$ [18,21–22]. In the EU project MASTER a range of threshold levels for locations with decreasing degree of protection was suggested [11]. Much higher threshold values are suggested for acetic acid: Tetreault [18] reports based on ASHREA guidelines [23] a "lowest observed adverse effect level dose" (LOAELD) of 1000 $\mu g/m^3/y$ (measured on copper coupons) should be valid for most cultural heritage materials and that concentrations below100 $\mu g/m^3$ are not mandatory due to generally high "no observed adverse effect level" (NOAEL) for objects. Thickett et al. [24] report a NOAEL for lead for concentrations below 317 $\mu g/m^3$, which is also used as the British Museum Performance Target for lead objects in display cases [18]. Sacchi and Muller report that "attempts have been made to set standard levels" resulting in a suggested low threshold level of 10 $\mu g/m^3$ for "conservation environments" [25]. This is in the lower range of typical outdoor background concentrations. Hatchfield [22] simply recommends the use of best available technology to control acetic acid concentrations. These recommendations are partly based on observed effects on metals. More research is needed about impact levels on especially organic materials.

4. Results

4.1. The Norwegian Institute for Air Research Early Warning Organic (EWO) dosimeter

Fig. 2 shows EWO results (absorption units at 340 nm) from inside and just outside of mc-frames in 12 locations (Table 1) and tolerable levels for different locations as derived in the EU project MASTER [10,11]. Measured values inside the mc-frames were in most instances very low. Nine out of 12 mc-frames were found to have acceptable conditions on the level of archive stores (Fig. 2). One location (SMK) is slightly above this level whereas two locations (NMK1 and MBV) are considerably higher, at the level of a historic house museum. There is large uncertainty (standard deviation of two samples) for SMK and EH K, indicating possible irregularities with these measurements. The EWO response for inside the mc-frame in transit with the SMK (not shown in Fig. 2) was 0.005, on acceptable level for an archive location. Measured values in the room locations show large variation, but are for all sites higher than the mc-frames. At one site (Tate S) a very low value acceptable for an archive store was observed. Eight out of 12 rooms showed values acceptable for purpose built or historical house museums. Two locations showed values acceptable for open displays in open museums whereas one location showed a value only acceptable for open displays with no control (Fig. 2).

4.2. The Birkbeck Piezoelectric Quartz Crystal (PQC) dosimeter

4.2.1. Resin Mastic Coated Crystals

Fig. 3 shows the responses of the RM-PQCs expressed in terms of frequency shift (Hz) / original coated crystal frequency (KHz). As in the case of the EWO dosimeter the responses are larger in the rooms than inside the mc-frames, except for one location (see Section 5).

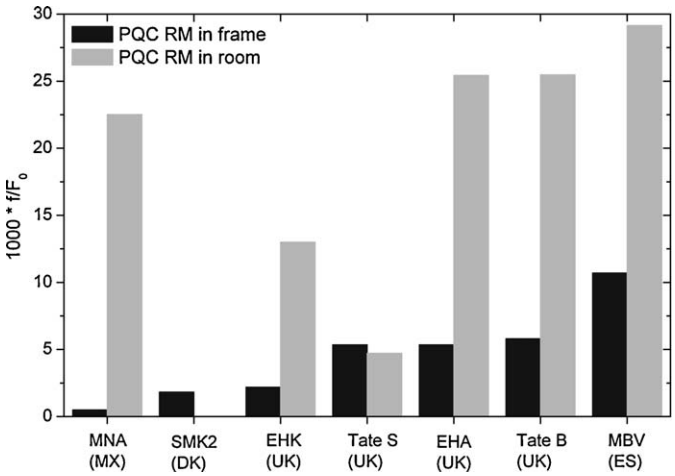

Fig. 3. Results from Resin Mastic Piezoelectric Quartz Crystal (RM-PQC). f / F_o = relation between the frequency shift and the original coated crystal frequency (KHz). For SMK2 measurement was not performed outside the mc-frame. The standard deviation for the measurements ranged from 0.66 to 1.0 with unit 1000 × f / F_o.

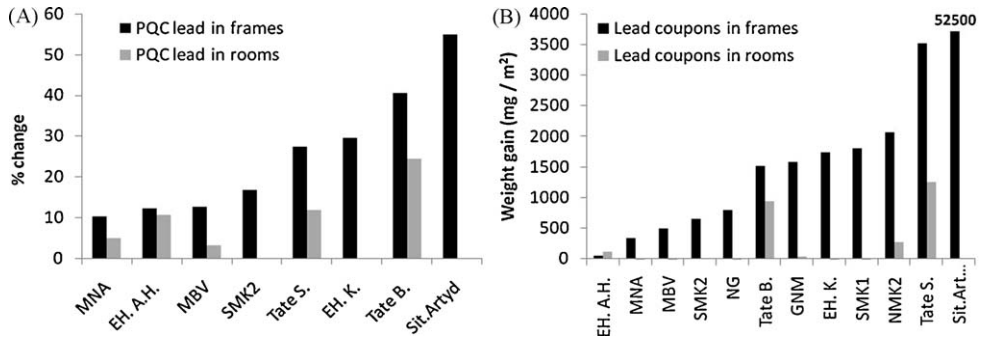

Fig. 4. A. Lead Piezoelectric Quartz Crystal (L-PQC) (Change (%) in frequency or mass) for selected site exposures: B.L lead coupons (weight gain / unit area) for site exposures. In the case of SMK2, EH.K and SIT-Artyd, measurements with L-PQCs were not performed in the rooms. For the other rooms no response was detected. The standard deviation for the measurements of the L-PQCs ranged from 0.12 to 0.22%.

4.2.2. Lead coated Piezoelectric Quartz Crystal crystals and lead coupons

The responses of the L-PQCs (calculated as percentage change in measured frequency or mass) and of the lead coupons (measured as weight gain / unit area) were higher inside the mc-frames than in the rooms for all locations except EH.A.H (lead coupons) where levels were very low both in the room and inside the frame (Fig. 4a and b). The largest response in the mc-frames was measured for the "worst case" at SIT-Artyd in Madrid.

4.3. The Fraunhofer Glass Slide Dosimeter

Fig. 5 shows the measured ΔE / Extinction values measured as IR absorption at 3300 cm^{-1} for the GSD. All measurements gave higher values inside the mc-frames than in the rooms, indicating higher pollutant concentration and degradation risk for vulnerable objects. Formates and acetates were identified by attenuated total reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) in the crystals observed on the surface of the dosimeter in the SIT-Artyd mc-frame, indicating that formic acid / formaldehyde and acetic acid were responsible for the high GSD value recorded in this mc-frame. Light microscopy of the glass surfaces from Tate B and Tate S was performed. A high concentration of surface "corrosion" crystals was observed from inside the mc-frames at Tate B and especially at Tate S. For Tate B wet crystal agglomerations greater than 50 μm in a three-dimensional spread were observed. For Tate S these crystals agglomerations were greater than 100 μm, partly covering and statistically distributed, locally with distinct edges. Outside the mc-frames statistically distributed crystal agglomerations lesser than 50 μm were observed for Tate B and small spots of wet crystals lesser than 10 μm at Tate S. No gel layer crack networks were observed on any of these glass surfaces.

4.4. Correlation of dosimeter results

Date directly correlating observed impact on the dosimeters with observed damage impact on the similar materials in real objects existed only partly. It was therefore decided to use available correlations between observed impacts on the dosimeters with recommended levels for environmental parameters to give damage thresholds for the dosimeters. Levels of tolerability of environments for organic-based archival and museum objects in different locations have previously been determined for the EWO [10,26]. Environmental impact levels, from acceptable to dangerous, for cultural heritage objects have been determined for the GSD [12,13]. Pairs of dosimeter responses, those of the EWO and RM-PQC (Fig. 6a) and those of the GSD and L-PQC (Fig. 6b), showed high correlation. These correlations allowed similar tolerable impact levels to be assigned also for the RM- and L-PQC (Fig. 6a and b). This corresponded to previous RM-PQC dosimeter calibration (light, NO_2).

4.5. Passive gas sampler measurements, temperature and relative humidity

The concentrations of organic compounds (acetic and formic acid, formaldehyde, TVOC) measured with passive samplers inside mc-frames were generally much higher than those for inorganic

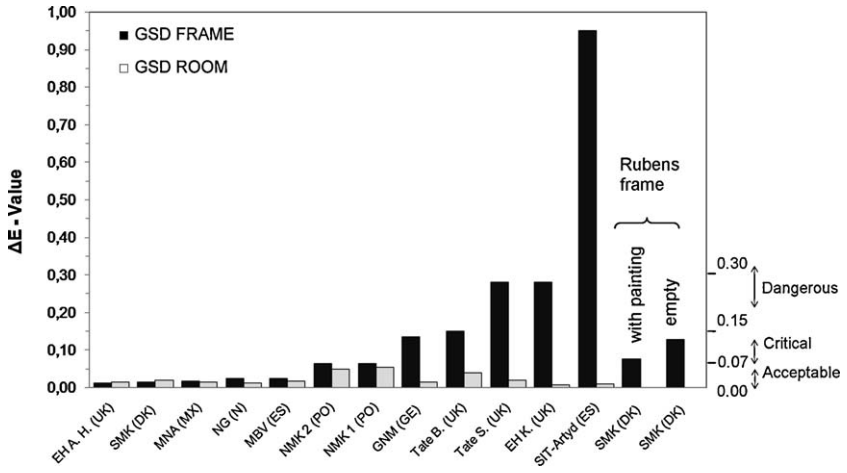

Fig. 5. Results from Glass Slide Dosimeter (GSD) (ΔE – Extinction values measured as IR absorption at 3300 cm^{-1}). (SMK = SMK1). Numbers in brackets are GSD impact levels: (1'): acceptable, (2'): critical, (3'): dangerous.

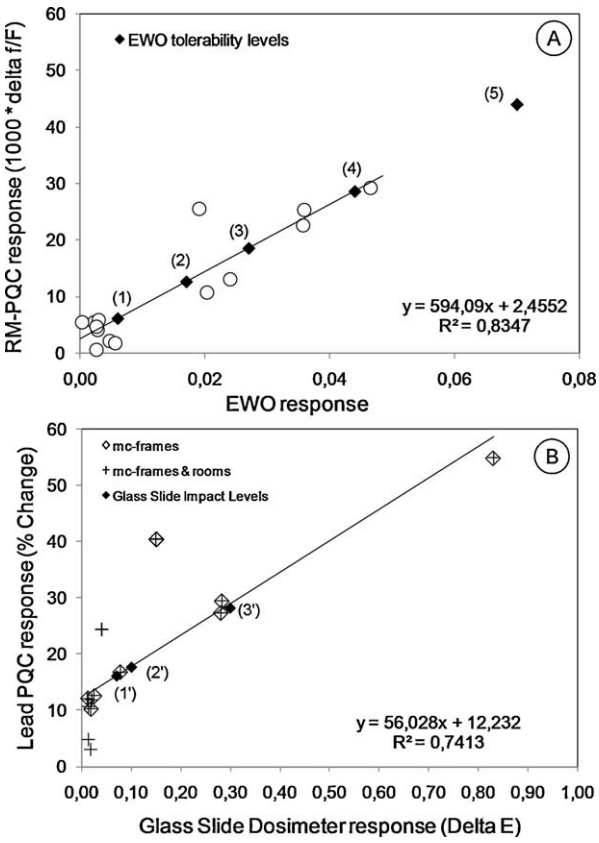

Fig. 6. Correlation between dosimeter responses in mc-frames and rooms. A. Early Warning Organic (EWO) and Resin Mastic Piezoelectric Quartz Crystal (RM-PQC) with locations tolerability levels (Fig. 2). B. Glass Slide Dosimeter (GSD) and Lead Piezoelectric Quartz Crystal (L-PQC) with impact levels (Fig. 5).

compounds (NO_2, SO_2, O_3). Organic compounds are emitted by the materials in the paintings (e.g. stretchers, panels and varnishes) and / or the materials used in the construction of mc-frames. Measurements inside the mc-frames showed acetic acid concentrations varying from 30 to 2000 $\mu g/m^3$, formic acid between 30 and 500 $\mu g/m^3$, formaldehydes between 1 and 6 $\mu g/m^3$ and total volatile organic compounds (TVOC) between 100 and 5000 $\mu g/m^3$. Inorganic gases, such as NO_2, SO_2 and O_3, are formed mainly outdoors and are ventilated indoors and into mc-frames. NO_2 and O_3 were measured in nearly all the mc-frames, varying between 1 and 5 $\mu g/m^3$ (Fig. 7) and 1 and 7 $\mu g/m^3$, respectively. SO_2 concentrations inside mc-frames were generally very low, below the

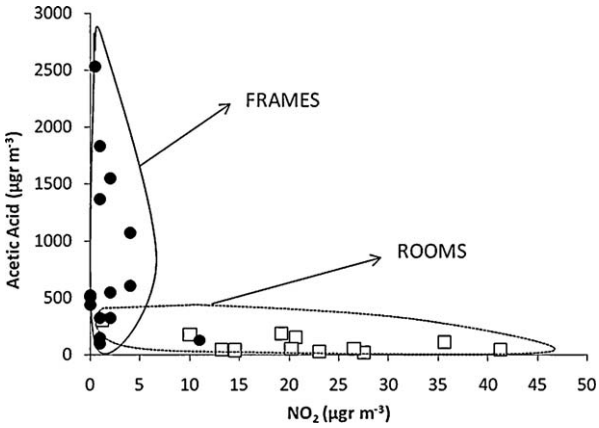

Fig. 7. Results for NO_2 and acetic acid concentrations.

detection limit (< 1 $\mu g/m^3$). The average standard deviation in measured concentrations and the standard deviation as percentage of average measured values were for NO_2; 0.8 $\mu g/m^3$ and 3.3%, for O_3; 1.0 $\mu g/m^3$ and 13%, and for acetic acid; 79 $\mu g/m^3$ and 16.4%. Fig. 7 shows the opposite patterns of measured concentrations of acetic acid and NO_2 inside the mc-frames and in the rooms, representing the typical difference between the organic and inorganic gases. A reduced humidity variation and increase in average humidity was measured for the mc-frames (mean RH from 38 to 59%) as compared to the rooms (mean RH from 25 – 55% RH), both of 9% RH. The mean temperatures in the mc-frames and rooms ranged from 15.2 to 21.9 °C, with an average of 17.8 °C, and from 15.6 – 21.7 °C, with an average of 18.8 °C, respectively.

4.6. Dose response relationships

Dose-response equations resulting from the statistical analysis are given in Table 2. The equations represent the best possible explanations for the combinations of all the used independent parameters satisfying the criteria of 95% significance (two-sided test). In cases where the constant in the equation was found negative or very large, of comparable size to the values for the dependent variable, the equation was fixed to the origin. For the EWO dosimeter a non-linear equation for polymer materials [26] was used. For the other dosimeters linear equations were derived.

Discussion.

The EWO measured very different photo oxidising impact inside and outside of the mc-frames. At two mc-frame locations relatively high values (NMK1 and MBV, Fig. 2) were measured. NMK1 (Table 1) was not an ordinary sealed mc-frame, but a more open glass enclosure over an opening in the wall in which the painting fitted. This arrangement did not give the same level of protection against the external environment as a well-sealed mc-frame. For MBV (Table 1) the measurement is unexpectedly high indicating some irregularity or lack of functioning for this mc-frame. However, the value for the room at MBV is also very high (Fig. 2) and could explain, at least partly, the high value for the inside of the mc-frame. For the room locations, the low EWO value measured in the conditioned Tate Store and the values on the level of historical house museums for nine other locations are expected (Fig. 2). Three locations (MBV, EH.A.H and MNA) show considerably higher values. These are central locations in relatively polluted cities where higher values can be expected, but depending on the protection effect of the building. The EWO measurements do, however, show that the control of pollutant infiltration, or possibly of climatic and UV conditions, in these museums is less than good.

The lower values for the RM-PQC in the mc-frames compared with the rooms similarly indicate the protective action of the mc-frames against oxidizing gases, and that the mc-frames may have shaded the dosimeters from light. The value for the RM-PQC dosimeters in the room in Tate S was much lower than for the room in Tate B (Fig. 3). This can be related to the difference in conditions. Tate S is air conditioned with filtered air, little human interference and low light levels. Tate B is an unconditioned stairwell space, exposed to central London pollution in a permeable building with single glazed wooden window frames. It has higher light levels and more externally generated pollutants. The similar result for mc-frame to the room at Tate S is probably due to the high ventilation rate of the mc-frame (Table 1). Measurement results for the L-PQCs and the lead coupons (Fig. 4a/b) clearly show correlation with measured values of acetic acid obtained from the passive samplers (Table 2). Values for crystal frequency change greater than 30 and high rate of change are indicative of a high-risk environ-

Table 2
Dose response equations for "PROPAINT-dosimeters". Grey shaded results are from a previous evaluation in the EU project MASTER.

Dosimeter	Dose-response equation	R^2	Removed data
1. EWO-linear	$EWO \times 1000 = 3.8 + 0.55 \times NO_2 + 0.82 \times O_3$	0.66	GNM-Room (one high parallel)
2. EWO-non-linear	$EWO \times 1000 = 3.8\ 3.9 + \sqrt{T}\ (0.12 \times NO_2 + 0.28 \times O_3)$	0.59	
3. EWO (EU project MASTER) Museum rooms	$EWO \times 1000 = 8.7 + \sqrt{UV} + \sqrt{T} \times (0.11NO_2 + 0.15O_3)$	0.73	
4. EWO (EU project MASTER) Showcases	$EWO \times 1000 = 4.5 + \sqrt{T}(0.16NO_2 + 0.052O_3)$	0.71	
5. RM-PQC	$RM\text{-}PQC = 0.61 \times NO_2 + 0.24 \times T$	0.92[a]	SIT (but little difference ± SIT)
6. GSD	$GSD \times 1000 = 0.20 \times AcAc$	0.75[a]	
7. L-PQC	$L\text{-}PQC = 7.4 + 0.017 \times AcAc$	0.83	Tate B – Room
8. Lead Coupons	$LC = 1.5 \times AcAc + 7.3 \times RH$	0.83[a]	SIT

EWO: Early Warning Organic Dosimeter; RM-PQC and L-PQC: Resin Mastic and Lead Piezoelectric Quartz Crystal Dosimeters; GSD: Glass Slide Dosimeter. Gas concentrations are in $\mu g/m^3$; AcAc: acetic acid; T: temperature (°C) and RH: relative humidity (%)

[a] For regression through the origin, the interpretation of R^2 is different and cannot be compared to R^2 for models which include an intercept.

ment for lead based objects. In another project exposure of lead coupons in 19 different museum environments showed a maximum value for weight gain in the range of 800 mg/m^2 [27]. This data suggests that levels above 1000 mg/m^2 should be taken as an indication of early warning of damage. In seven of the 11 mc-frames measured values above 800 mg/m^2 (six above 1000 mg/m^2) were measured. Two of the room locations (Tate S and Tate B) yielded values above 1000 mg/m^2. The value obtained from inside the "worst case" mc-frame at SIT-Artyd (Fig. 4b) provided a good example of maximum damage. This was observed as a high level of alteration of the surface and high value for weight increase.

The GSD results (Fig. 5) similarly indicate that the microclimate in the SIT-Artyd "worst case" model mc-frame is characterized by a very high "dangerous" pollution concentration. The high values observed inside the mc-frames at EH K, Tate S, Tate B, GNM and SMK1 were probably, as with the L PQC and lead coupons, due to organic emissions such as formaldehyde and acetic acid. This was supported by the presence of such salts in the surface crystals on the dosimeter exposed at the SIT-Artyd location.

The GSD M1.0 with fire polishing finish, for which values are reported in this paper, showed best linear and sensitive behaviour of the several types of GSDs exposed, as was expected.

The impact doses of pollutant gases on paintings in the mc-frames are expected to be a combination of the oxidants ($NO_2 + O_3$) and the organic (acetic and formic) acids that are present in measurable and sometimes high concentrations. All the dosimeters used were found to be sensitive to only one of these two groups of compounds (Table 2). The higher levels (Figs. 2 and 3) generally measured in the rooms than in the mc-frames by the EWO and RM-PQC can be explained by higher NO_2 (Fig. 7) + O_3 concentration and more light / UV in the rooms. The reason for the lower R^2 for the EWO equation (Table 2) may be the lack of UV data for the room locations. In previous studies the EWO and RM-PQC were found to be sensitive to light / UV [14,15]. UV data were included in EWO-MASTER equations (Table 2; gray shaded). The inside to outside of the mc-frames ratios (I / O ratios) for the impacts on the EWO and RM-PQC, and for NO_2 concentrations, did not show simple correlation with the measured ventilation rates (Table 1). This may be due to different deposition fluxes of the pollutant gases to the mc-frames and different light conditions at the locations of the dosimeters inside the different mc-frames. Unlike the EWO and RM-PQC, the GSD and L-PQC are sensitive to acetic acid and measure higher impacts inside the mc-frames (Figs. 4 and 5).

Whichever threshold levels are considered for the inorganic oxidants (NO_2 and O_3) and the organic acids (formic and acetic), the combined impact of the pollutants needs to be evaluated. Many different species of VOCs are emitted and can be detected inside mc-frames [28]. However, since little is known about possible degradation effects on paintings of these diverse species, at present for the general assessment of the quality of environments in mc-frames, measurement of effects of organic (acetic and formic) acids seems the best option. In the location-tolerability diagrams (Fig. 8a and b) the results from the RM-PQC (oxidizing impact) and L-PQC (acidic impact), and from the EWO (oxidizing impact) and GSD (acidic impact), are plotted with the threshold levels given from Fig. 6a and b. The three lower "tolerability location levels" (1–3) for the EWO were all set equal to the lower "impact level" (3) for the GSD, assuming a NOAEL in line with Tetreault [18].

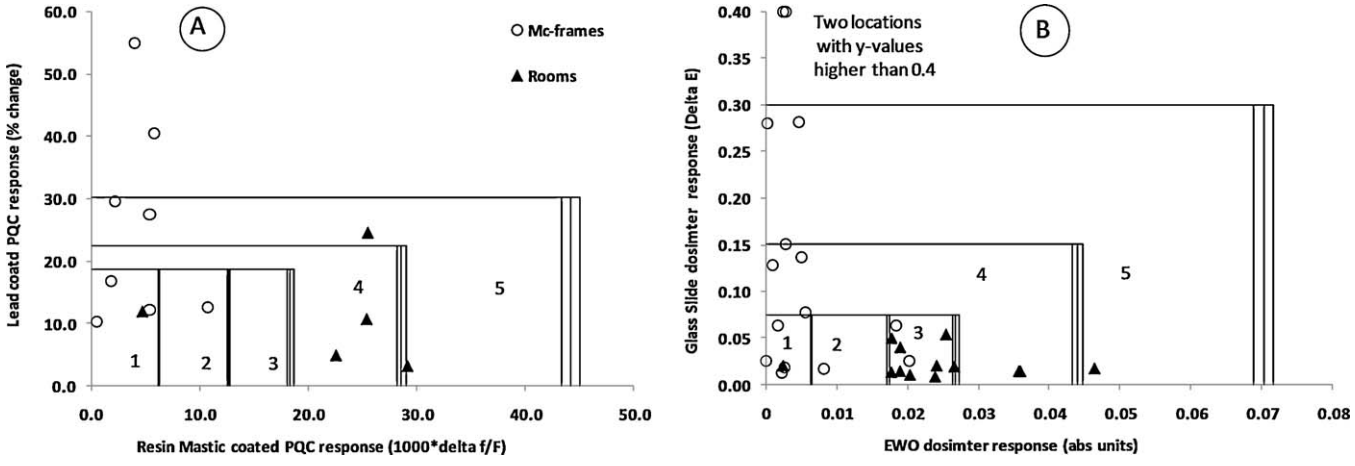

Fig. 8. Location-tolerability diagrams with threshold values (Fig. 2) for cultural heritage objects in indoors locations. A. Results from Resin Mastic Piezoelectric Quartz Crystal (RM-PQC) (x-axis) and Lead Piezoelectric Quartz Crystal (L-PQC) (y-axis) (Figs. 3 and 4) and B. from Early Warning Organic (EWO) (x-axis) and Glass Slide Dosimeter (GSD) (y-axis) (Figs. 2 and 5). The close vertical lines are the relative humidity dependence for each level.

The three upper "tolerability location levels" (3–5) for the EWO were set equal to the three (1–3) "impact level" for the GSD. It is important to stress that such threshold values are based on limited knowledge and evaluation of severity of impact and on currently available measurement technology, – and thus may change in the future. The distinction between the locations inside the mc-frames and in the rooms is clearly seen in Fig. 8a and b. Deviation from the best level, no. 1, is mostly in the direction of higher EWO and RM-PQC values for the rooms and in the direction of higher GSD and L-PQC values for the mc-frames, in agreement with the pollutant measurements (Fig. 7). The EWO and RM-PQC generally measured good conditions in the mc-frames. Only three EWO and one RM-PQC results were higher than level 1. However, in many of these locations high GSD or L-PQC values were measured, indicating level 4, 5 and worse (Fig. 8a and b). Thus, for most of the mc-frames internal emissions and high deposition fluxes of organic, and especially acetic, acid is the main concern. The major potential pollution risk to paintings in mc-frames is probably the trapping of organic acids. It is therefore very important to establish impact and risk levels, such as those in Figs. 6 and 8, with greater certainty. Most room locations were found to be in levels 3 or 4. All the rooms (except Tate B with high values for the L-PQC) were found to be in level 1 for the acidic effects. Thus, the main problem in rooms is the oxidizing species infiltrated from outdoors.

Dosimeters integrate several pollutant and climate effects (Table 2), and respond to the actual air-flow conditions and fluxes of the pollutants on the objects. Therefore dosimeters may give a better measure of degradation effects on objects than individual measurements of pollutants.

6. Conclusion

The dosimeters used in PROPAINT clearly have complementary properties measuring damage either from photo-oxidising or acidic influences. The EWO and RM-PQCs are sensitive to inorganic and oxidizing pollutant gases which result from the ingress of outdoor pollutants into indoor environments and into mc-frames. The GSD and L-PQCs are highly sensitive to effects of organic acids emitted and trapped within mc-frames. High doses [18] of acetic acid inside well-sealed mc-frames may pose a risk to paintings. The combined use of two or more dosimeters with complementary properties gives a good measure of the quality of the environment and the expected risk for paintings in mc-frames.

There is currently an increased trend to use mc-frames to protect paintings in museums and galleries, for display, transit and in storage. The high doses of acetic acid found inside well-sealed mc-frames may pose a risk to paintings housed in this way. It is very important for the long-term preservation of paintings (and other objects) that damaging threshold levels for organic, and especially acetic, acid are determined. There is a clear need for complementary measurements to establish dose-response relationships for the effect of organic acids on varnished and non-varnished paintings. This would make it possible to determine how the conditions in mc-frames, with lower levels of oxidants (NO_2 and O_3) and higher levels of organic acids, affect their long term preservation and answer the question whether mc-frames should be well sealed or ventilated.

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