

Development of damage functions for copper, silver and enamels on copper

David Thickett, Rebecca Chisholm and Paul Lankester

Abstract

This paper describes the development of damage functions for silver, copper and enamels using different representative environments in five historic buildings with a wide range of environments.

The copper and silver corrosion rates were determined from Purafill Onguard 3 piezo-electric quartz crystals coated with copper and silver. The thermal deterioration of enamels has been of concern in conservation for some time. Such deterioration, occurring at the metal/glass interface, is difficult to assess visually. Acoustic emission is an extremely sensitive technique that can detect micro-cracking in rigid materials. Its use for enamels has been developed through a series of simple experiments. It was found that events are generated from the development of cracks, as small as 1 micron in length, at the metal/glass interface. A series of experiments in showcases with sensors attached to replica enamels with a conductive gel derived the damaging level of thermal shock, below which acoustic emission was not detected. Replacing the tungsten lighting with LEDs reduced the thermal load and no longer caused acoustic emission. Monitoring of historic enamel plaques (without the gel) replicated these results. Two correlation methods were used to remove environmental noise.

Damage functions are normally developed from periodic measurements of a material's deterioration and a multivariate fit to environmental data. There are questions about how to deal with semi-continuous data such as temperature and relative humidity for this process. Semi-continuous measurement is now available for some damage types such as the Onguard copper and silver piezo-electric quartz microbalances, resistance-based metal sensors and acoustic emission. The high sensitivity of these devices allows data to be collected at the same measurement interval as temperature and relative humidity logging (30 or 60 minutes).

The development of damage functions provides an improved way to assess environmental data. It can allow a move towards more targeted standards, defining equal risk of deterioration, instead of the present prescriptive approach.

Introduction

The interpretation of environmental monitoring data in terms of risk to artefacts is a complex task. In historic buildings, the temperatures, relative humidities and pollution levels are much more influenced by external conditions than in air-conditioned spaces. The fluctuating environments encountered complicate the process significantly. In many institutions this assessment is undertaken by considering published materials science and experiences of the collections' previous response. Damage functions can allow a better-informed assessment and, if

developed under appropriate exposures, can accommodate fluctuating conditions.

Damage functions for copper and silver

Damage functions were investigated for silver and copper in historic house environments. The silver and copper tarnish rates were measured using Purafil Onguard 3 loggers. The Onguard 3 logger uses piezo-electric quartz crystals coated with either silver or copper. The crystals resonate at exactly 6 MHz. As their mass increases the resonant frequency decreases and the mass can be related to the frequency shift by the Sauerbrey equation. Purafil converts the mass increase to a tarnish layer thickness using an averaged tarnish layer composition and density for silver and copper. This technique is known to be temperature sensitive and the Purafil system includes circuitry to compensate for temperature differences. This is reported to be inadequate and a simple numerical correction has been proposed, which was used in this work [1]. The logger also records temperature and relative humidity. The crystals are covered with a perforated clear plastic cover (to physically protect them from handling). This has some impact on dust deposition on to the crystals.

Onguard 3 loggers were placed in seven locations in five properties for three years. The properties were selected to give a range of environments found indoors. The environments are described in [table 1](#).

The properties are in very different environments: relatively polluted, clean, urban, rural and maritime. At Apsley House the different types of mechanical conditioning in rooms give very different environments. The Waterloo Gallery has a full air-conditioning system with activated charcoal filtration, having low pollution levels (compared to the environment). The Plate and China Room has mechanical ventilation with no chemical filtration and has high pollution levels due to the very close proximity of an extremely busy road junction. The Dining Room is naturally ventilated and falls between the two other rooms at Apsley House.

Table 1. Conditions in seven rooms in five properties used for the exposure trials

Location	Amount of time in RH band (%)						Max NO ₂ ppb	Max SO ₂ ppb	Max O ₃ ppb	Max HCl ppb	Max H ₂ S ppb	Max dust % coverage in 30 days	Max Cl deposition rate mg/m ² -day
	< 40 %	40-50 %	50-60 %	60-70 %	70-80 %	> 80 %							
Apsley dining room	1.0	41.7	46.7	9.9	0.5	0.0	16.4	0.4	0.7	0.6	0.29	1.34	9.1
Apsley Waterloo gallery	52.8	34.4	12.1	0.7	0.0	0.0	11.6	bd	5.7	1.0	0.02	0.28	1.0
Apsley plate and china room	0.0	57.3	30.9	10.3	1.5	0.0	21.2	0.1	8.9	1.4	0.31	2.13	15.6
Rangers bronze room	16.0	35.9	29.1	12.6	5.5	0.6	8.9		1.9	1.2	0.17	0.16	3.8
Brodsworth dining room	0.0	2.3	18.8	37.5	36.3	5.1	4.2	0.4	12.1	0.8	0.05	0.17	1.6
Audley End dining room	0.0	15.4	48.0	36.6	0.2	0.0	2.0	0.2	5.0	2.0		0.24	1.3
Walmer dining room	1.3	18.7	31.1	20.8	25.4	2.6	3.6	0.2	7.1	0.9	0.13	1.14	94.4

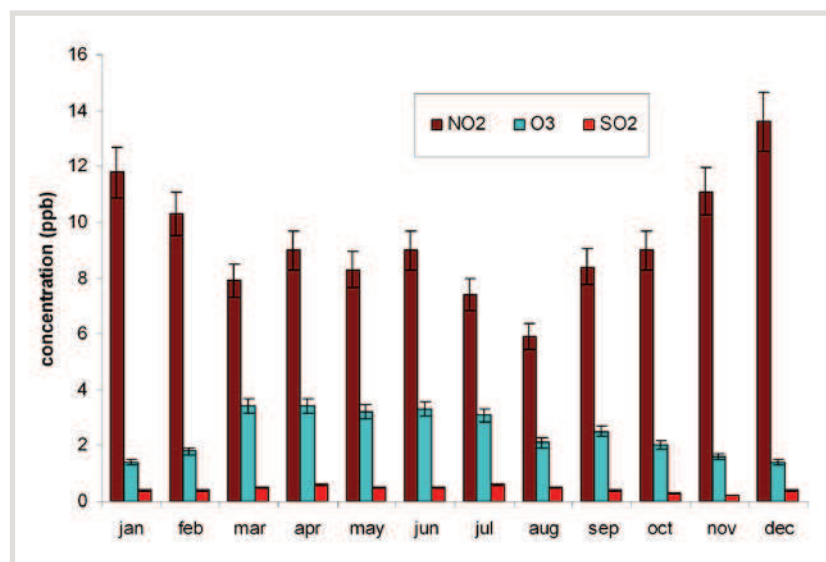


Figure 1. Monthly nitrogen dioxide, sulphur dioxide and ozone concentration at Rangers House

Pollution measurements were taken with diffusion tubes for four 30-day periods, one in each season per year, a total of twelve in the three-year monitoring period. Previous annual measurement campaigns at Rangers House, Chiswick House and Brodsworth Hall (with sequential monthly measurements) had validated this approach as representative of the pollution levels for nitrogen dioxide, ozone, and sulphur dioxide. Figure 1 and table 2 show the data for Rangers House.

The doses calculated from all the data and using one month from each quarter are shown in table 2. The doses calculated from using the four quarterly month periods are within 7.7 % of those calculated from all the twelve months data. This is well within the errors for the diffusion tubes used.

The pollutants nitrogen dioxide, ozone, hydrogen chloride (measured as deposited chloride) and hydrogen sulphide were measured. The method for the commercially available hydrogen sulphide diffusion tube analyses was changed towards the end of the exposures, increasing the detection limit beyond that found in the properties and an alternative method devised by Ankersmit was used [2]. This involved exposing a cleaned silver disc in the end of a diffusion tube. After exposure the amount of silver sulphide on the disc was analysed using cyclic voltammetry [3]. This amount was related to the airborne concentration of hydrogen sulphide using the published empirical calibration.

The monthly silver and copper tarnish rates from the OnGuard 3 loggers were regressed against the environmental data using the Minitab software package [4]. The regression equations calculated were for:

Silver

$$Ag = 45.30 HS + 1.46 NO + 3.90 SO + 4.81 HCl + 0.20 O_3 + 1.04 RH + 0.79 T$$

where

Ag is the silver tarnish rate in Å (0.1 nm) per 30 days

HS is the hydrogen sulphide concentration in ppb

SO is the sulphur dioxide concentration in ppb

HCl is the hydrogen chloride concentration in ppb

O₃ is the ozone concentration in ppb
 RH is the mean RH, %
 T is the mean temperature, °C

Hydrogen sulphide has a very strong influence on the silver tarnish rate, with hydrogen chloride and sulphur dioxide also having some effect and the other environmental factors less so.

Copper

$$Cu = 5.71 HS + 0.35 NO + 7.30 SO + 2.09 HCl + 1.24 O_3 + 0.17 RH + 1.00 T$$

where Cu is the copper tarnish rate in Å per 30 days.

Copper tarnished to a much lower degree than silver; hydrogen sulfide has the strongest effect, followed by sulfur dioxide (although it is now present at very low levels in many western European locations), followed by hydrogen chloride, then ozone.

The damage functions cover a wide range of environments (Table 1) and should be suitable for use in many heritage situations. The lack of commercially available carbonyl sulfide sensors or diffusion tubes is limiting. Measurements in museums often detect carbonyl sulfide concentrations around three times the hydrogen sulfide concentration. Figure 2 shows a set of data from a London museum gathered from measurements by Oxford Brookes University with a diffusion tube method.

Although silver is reported to be less sensitive to carbonyl sulphide than hydrogen sulphide, the higher levels mean it is likely to have a significant effect, unconsidered in the damage function. Additionally, dust is known to have a significant effect on silver tarnish and has not been considered in this work due to the design of the OnGuard sensors, which significantly reduce dust deposition [5].

The OnGuard 3 loggers' batteries failed during some measurement periods over the summers (there is a battery indicator but it appears to be inaccurate at battery levels below 30 %; one logger failed during the exposures and had to be repaired). Hence although the data includes mean temperatures above 20 °C, there is not a representative amount of data for the higher temperatures. Figure 3 shows the mean temperature plotted against copper tarnish rate. The damage functions derived may not fully account for the higher temperature periods.

Damage functions for enamels on copper

Many of the decay mechanisms of interest result from fluctuations in relative humidity or temperatures. These vary enormously in

Table 2. Annual doses of pollutants calculated from 12 monthly measurements and estimated from subsets of the data

Dose ppm.month	Calculated from all data	Calculated from Jan, Apr, Jul, Oct	Calculated from Feb, May, Aug, Nov	Calculated from Mar, Jun, Sep, Dec
Sulfur dioxide	6.5	6.6	6.0	6.9
Nitrogen dioxide	108.5	108.9	102.8	113.7
Ozone	26.2	26.6	24.7	27.2

many heritage environments. Figure 4 and 5 show the distribution of daily temperature fluctuation and maximum rate of temperature change for a showcase containing Limoge enamels. The data is taken from a year's monitoring, with some gaps due to poor data transmission of the radiotelemetry system used.

There is a lot of variation in the data. Dealing with different rates of change has been recognised to be important in object response [6,7], but little work has been published on how to process such data.

Enamels are known to be susceptible to damage by temperature fluctuations. De-bonding at the glass/metal interface is particularly problematic as it makes the enamel much more susceptible to further damage. It is also difficult to detect such de-bonding visually.

When rigid materials are flexed, micro-cracks occur. This process is accompanied by acoustic emission, which is high-frequency sound generation. Acoustic emission has been utilised for monitoring wooden furniture and panel paintings and the expansion of sulfate salts in stone [8 to 10]. Application of the technique has been investigated for enamels under thermal stress. Initial work was carried out as part of an MA research project by Jenny Studer between English Heritage and the Royal College of Art and has been reported [11].

Figure 2. Hydrogen sulfide and carbonyl sulfide concentrations in a London museum

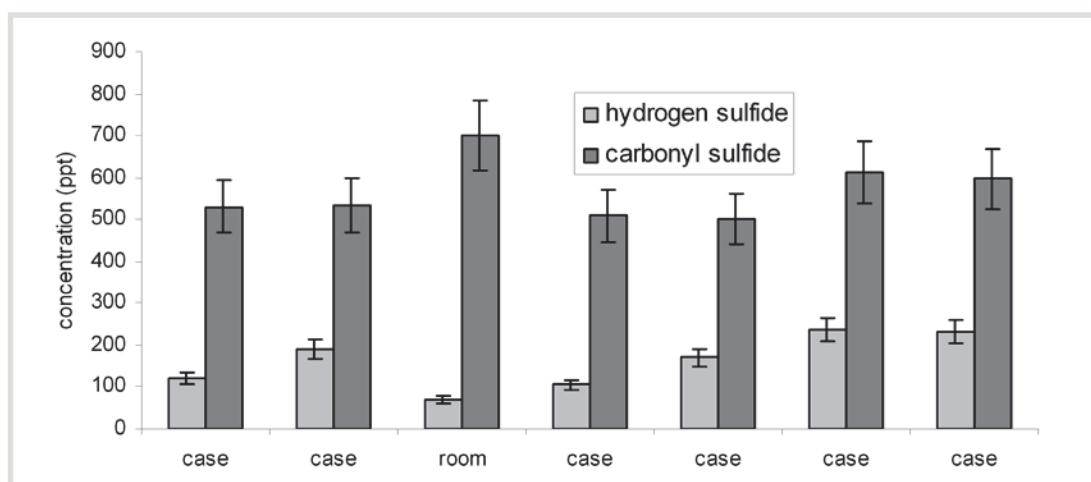
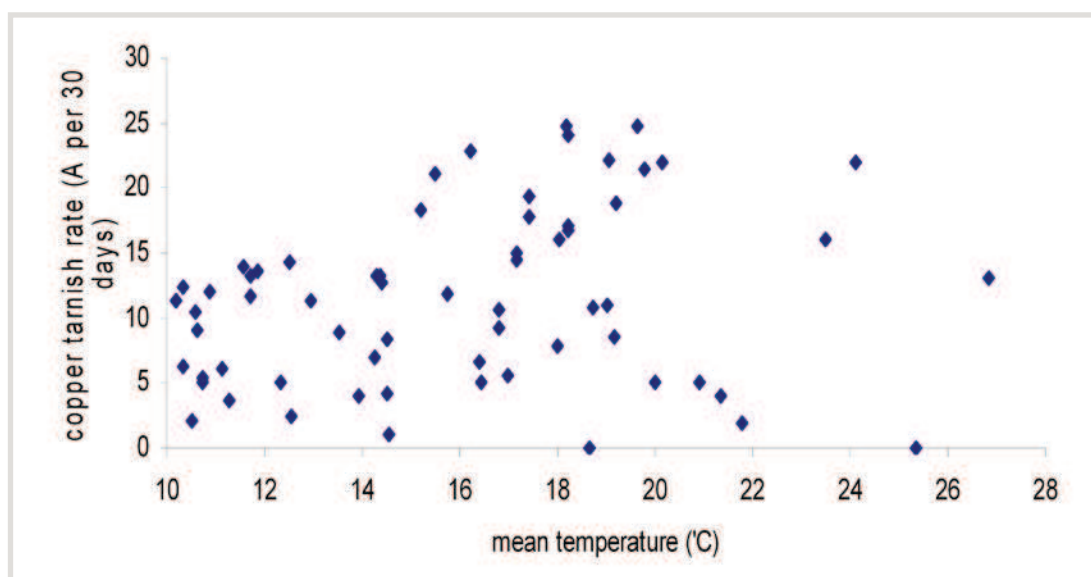


Figure 3. Copper tarnish rates and mean temperatures of measurements used to derive the damage function



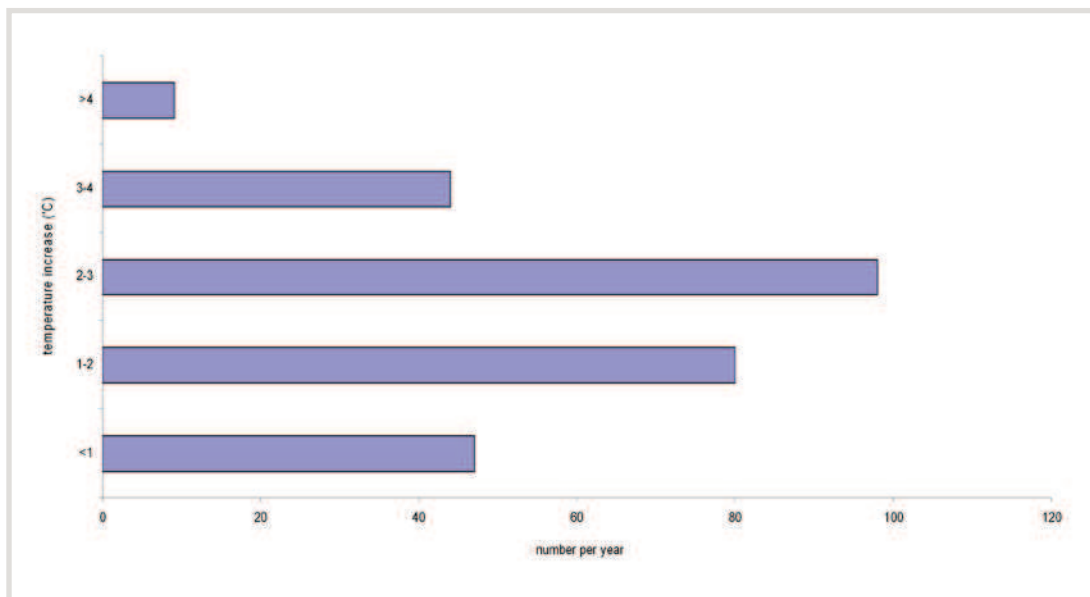


Figure 4. Distribution of daily temperature fluctuations in the Limoge enamel case at Rangers House, London

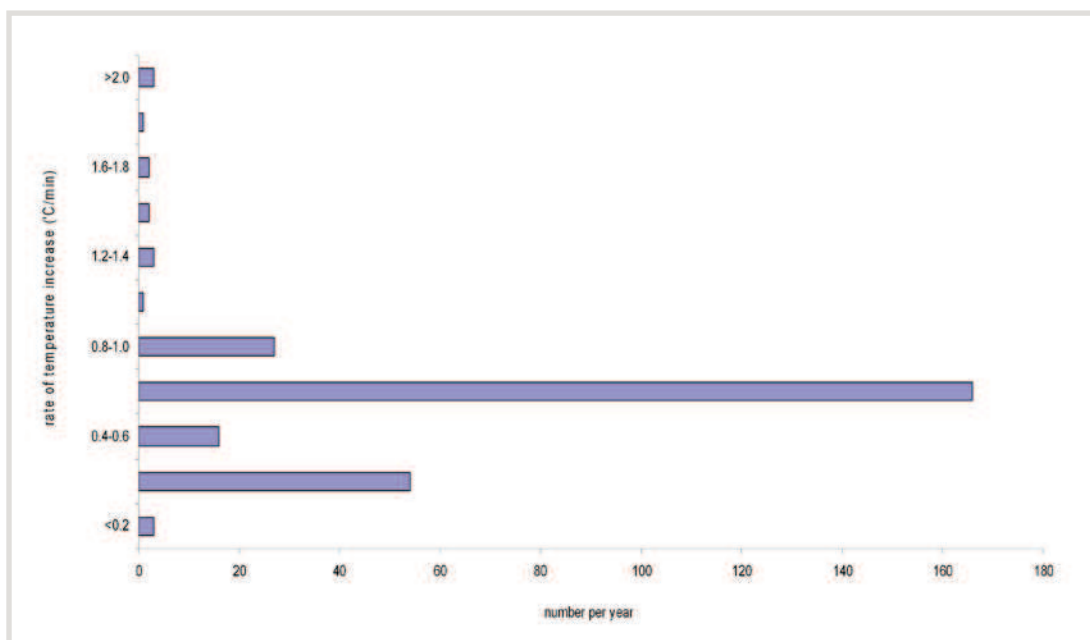


Figure 5. Distribution of maximum rate of change of temperature in that case

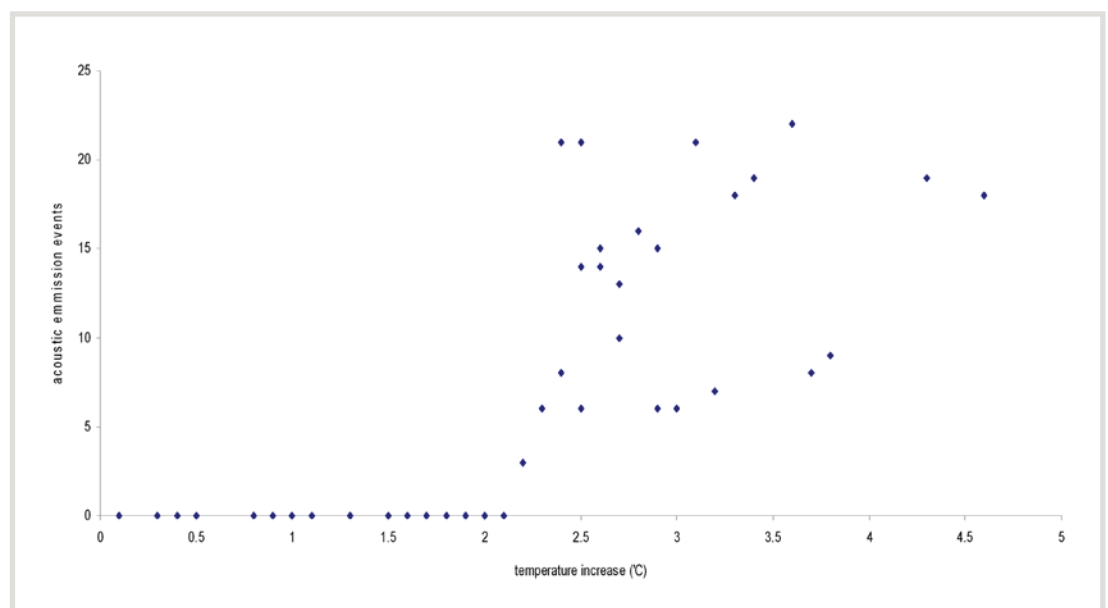
A physical acoustics Pocket AE2 with R15 α (1 kHz to 1 MHz, plus/minus 1.5 dB) sensors was used throughout this work. Simulated weathered enamels were kindly provided by Veerle Van der Linden and Eva Annys, Royal Academy of Fine Arts, University of Antwerp, Belgium. Two sets of experiments were carried out. The enamel pieces with acoustic emission sensors held in contact with rubber bands and with and without a contact gel (Sil-Glyde $\text{\textcircled{c}}$) were submitted to three-point bending tests and heating a water bath to 43 ^\circ C . The enamel pieces had been pre-weathered and contained several cracks already. In several tests these were marked with black ink and the pieces examined for any new cracks under magnification after the first acoustic emission event in three-point bend tests. The minimum detectable crack length was assessed to be 1.2 μm with the contact gel and 3.1 μm without it. The initial tests had only detected crack lengths of 1.46 mm, indicating the technique would only detect very severe damage, the further tests confirmed its utility to detect the early stages of damage. Acoustic emission was observed in both tests, indicating the method was suitable for monitoring enamels.

Rangers House in Greenwich, London displays the Werner Collection, which includes many Limoge enamels. The collection is on a hundred-year loan to English Heritage. Four showcases contain large numbers of enamels. The custom-built showcases are lit with both fibre-optic and tungsten lighting. The temperature distribution in the narrowest enamel showcase was assessed using eight temperature probes (ACR SR002 loggers with EH-020 A extension probes). Probes were placed in the centre and edge, back and front, top and bottom of the 1.6 m by 1.2 m by 0.4 m case. The edge and centre probes gave very similar readings. A 4.5 K temperature rise at the top front of the case nearest the tungsten lights was recorded, this reduces to 2.7 K at the bottom back. Full details have been published [13]. Thermal imaging (Inframetrics ThermaCam PM290) indicated a temperature gradient of up to 2 K across the surface of some enamels.

Acoustic emission measurements were carried out on both the simulated enamels with contact gel and the objects without contact gel. Experiments with a variety of inert materials showed Melinex sheet (50 μm , non-coated) gave the best (closest to the contact gel) results and this was used between the acoustic emission sensor and glass or metal of the enamels. The deflection of the enamels was measured with a laser transducer (Acuity AR600) to capture the movements causing any micro-cracking. Environmental noise is an issue with acoustic emission and several approaches are available to correct for it. For wood, anti-correlation measurements with two sensors attached to the wood over 6cm apart have been used [8]. The acoustic signal will not travel more than 6 cm in the wood, hence signals measured at both sensors are environmental noise, whereas a signal measured at one sensor only is assumed to be due to acoustic emission from the wood. The signal transmission through copper was measured on a 2 mm copper sheet. This was found to be over 30 cm, larger than most of the Limoge enamel plates being investigated. Two measurement geometries were used.

- One sensor pressed against the enamel glass surface using a g-clamp and Melinex between the sensor and the glass. A second sensor pressed against the backboard of the case (on which the

Figure 6. Acoustic emissions from enamel plaque plotted against daily temperature fluctuation



enamels were mounted). Acoustic emission was assumed to originate from the enamel if only the enamel sensor measured a signal.

- One sensor pressed against the front glass of the enamel, a second pressed against the back of the enamel. The difference in measurement time was used to locate where the signal originated from. Experiments with the simulated enamels were used to determine the transit times of signals through the enamel. Shorter time difference signals were assumed to have originated in the enamel.

The measurements showed significant acoustic emission originating from the enamel plaques during the daily heating cycle within the showcases. This evidence was used to argue for funding to change the lighting. The tungsten lamps were replaced with LED lamps. This reduced the temperature gains significantly and there was no longer any detectable acoustic emission, even from the simulated enamel samples with contact gel enhancing the sensitivity of the technique. The daily temperature increase in the showcases with the new lamps was less than 1.4 K.

The data set generated by acoustic emission from the simulated enamels and the temperature profiles causing that emission provide an ideal opportunity to assess threshold thermal fluctuations. Unfortunately, the visual impact of the sensors in front of the enamel plaques limited the duration of these experiments to a couple of daily cycles and most data were from the replica plaques, but some real plaque data were available to check the results. The number of acoustic emissions versus the air temperature increase is plotted in [figure 6](#).

There is a threshold at a temperature fluctuation between 2.1 and 2.5 K (considering the errors in the method). The LED lamps generated daily fluctuations of less than 1.4 K, well below this value.

Surface temperature would be a better measure for this than air temperature, particularly as the tungsten lamps produce an infra-red radiance of 3.3 mW/m² at the highest points in the showcases where enamels are displayed. An accurate measurement would require attaching a surface temperature sensor to the front glass of the enamel, which would be visually intrusive for long-term monitoring. Infra-red surface temperature measurement would be extremely difficult for the enamel plaques in the showcases due to the narrow case geometry.

Damage functions with continuous data

Damage functions are normally developed from periodic measurements of a material's deterioration and a multivariate fit to environmental data. The periods tend to be quite long as materials deteriorate slowly and the measurements can be resource-intensive. Pollution data are most often collected using diffusion tubes, exposed for weekly to monthly periods. The difference in period makes the fit for the damage function difficult and pollution data often have to be accumulated. Temperature and relative humidity are normally collected at half-hourly or hourly intervals during exposures. Mean values are generally used for the multivariate fits. Both variables are rarely normally distributed, particularly in indoor environments, therefore using the mean may

be problematic. Additionally, the deterioration of many materials is known to follow parabolic or power laws for relative humidity, and mean values can seriously underestimate the effect [12].

More sensitive analytical methods have been developed and can be used to reduce the period between damage measurements, homogenising the data sets. Semi-continuous measurement is now available for metal corrosion, such as the Onguard copper and silver piezo-electric quartz microbalances and resistance-based metal sensors [14]. The high sensitivity of these devices allows data to be collected at the same measurement interval as temperature and RH logging (30 or 60 minutes). The precision for the Onguard technique is 1 Å, which relates to 10 hours of corrosion in the most aggressive environment measured. The tarnish rates measured for silver varied between 1 Å per week and 16.5 Å per week. The Onguard 3 output is not precise enough for a regression on a 30-minute time period. However the frequency shifts of the piezo-electric quartz crystals are much more precise with a 1 Å increase in silver tarnish equating to a 39 Hz frequency drop. The frequency shift data was extracted from the Onguard 3 loggers and more precise silver and copper tarnish rates calculated.

At four locations in Apsley House and Brodsworth Hall continuous loggers for ozone (Teledyne API M400E), nitrogen dioxide (200EU) and sulphur dioxide (2100E) were located in the rooms with the Onguard 3 loggers for two weeks each. No continuous monitors were available to the project for hydrogen sulphide or hydrogen chloride gases. Hydrogen sulphide continuous analysers can be made by adding a convertor to a sulphur dioxide analyser and fluorometric [15] and lead acetate tape-based analysers are also available. The 30-minute tarnish rates were regressed against the pollution, temperature and RH values as before.

Silver

$$Ag = 0.08 NO + 0.86 SO + 0.06 O_3 + 0.33 RH + 2.77 T$$

where

Ag is the silver tarnish rate in Å per 30 days

SO is the sulphur dioxide concentration in ppb

NO is the nitrogen dioxide concentration in ppb

O₃ is the ozone concentration in ppb

RH is the RH, %

T is the temperature, °C

Temperature has a very strong influence on the silver tarnish rate, with sulfur dioxide and RH also having some effect and the other environmental factors less so. The damage function was derived from 5376 measurements, compared with 78 for those derived previously from monthly measurements. Hydrogen sulphide and hydrogen chloride were not measured and hence do not appear in the damage function. It is not possible to compare these short-term damage functions with those derived previously due to this discrepancy.

Copper

$$Cu = 0.01 NO + 0.35 SO + 0.30 O_3 + 0.49 RH + 0.44 T$$

where Cu is the silver tarnish rate in Å per 30 days.

RH, temperature, ozone and sulphur dioxide all had similar influences on the copper tarnish rate, nitrogen dioxide much less so and this was only just significant at a 0.05 % level in the regression.

Approaches to uncertainties

The figures produced by damage functions have limited value without an estimate of uncertainty attached. This aspect has not, on the whole, been addressed in the published literature on damage functions. A number of approaches are feasible.

Where large amounts of data are available (such as the real-time measurements described in the 'Damage functions with continuous data' section above, the data can be split into a calibration and verification set. Ideally, the calibration set should range beyond, or at least as far as, the verification set in all the parameters used in the damage function. The values should also ideally be evenly spread over the range. The damage function can be developed from the calibration set and then used with the verification set at each group of variables. The estimated damage can then be compared with the measured damage for that set of values and errors calculated.

Large data sets are often not available due to the relatively long time periods required for accurate object-response measurements. For example, the raw Oguard output could not be accurately used for time periods below three weeks. The monthly data presented has 78 sets of data, which is approaching the bare minimum for the calibration/verification approach. An alternative is to treat the damage function as a multivariate linear calibration. The uncertainty can be estimated from the error estimates in the measurement parameters. In this study plus or minus 0.1 K for temperature, plus or minus 1 % for relative humidity (high accuracy probes were used), plus or minus 6.9 % to plus or minus 10.3 % for the diffusion tube analyses (depending on the gas analysed, this can vary with the method). The error estimates are then combined with the error of the slopes and intercept values from the multivariate calibration to estimate the overall uncertainty at each calculated value.

Further work

The data will be further analysed using the partial least squares method. Correlation between the x-variables (environmental data) can cause multiple linear regression to fail. Environmental data is often collinear and especially so in this instance with high humidity and all the pollutants ingressing from outside the properties. This ingress depends on atmospheric conditions (which influence pressure differences and air exchange rate) and open doors; high air exchange rates will transport all the pollutants. Partial least squares is not sensitive to collinearity and calculates components which effectively describe the covariance structure of the x data matrix [16].

The exposures will be continued for a further year to collect enough summer data. At the end of the exposure period, the tarnished silver and copper crystals will be analysed with x-ray fluorescence spectroscopy and cyclic voltametry to determine the tarnish layer composition. The composition will be compared with

the average value used by Purafil to determine the layer thickness and the values corrected if necessary. The resistance-based Musecorr sensors are about to become commercially available. A subset of the work will be repeated with them to determine the effect of dust deposition on the damage functions.

The acoustic emission method will be trialled with bone and ivory to determine their response to fluctuating relative humidity.

Acknowledgements

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