REACTIVITY MONITORING OF ATMOSPHERES

D Thickett*, R Chisholm, P Lankester

English Heritage
Rangers House
Chesterfield Walk
London
SE10 8QX
UK

*Corresponding author: david.thickett@english-heritage.org.uk

Abstract

Knowledge of metal corrosion rate is essential for managing heritage environments. Information about the type of corrosion can help to identify the source of observed corrosion problems. Metal corrosion is influenced by a wide range of factors and monitoring all the relevant parameters can be challenging. Even if all the relevant parameters for an environment are measured the research knowledge base that is available to assess the results is incomplete.

Reactivity monitoring by measuring the corrosion rate of metal pieces can provide an efficient way to monitor environments. This paper reviews the use of this method, identifying advantages and disadvantages for different situations. The influence of the most important parameters (metal composition, surface preparation and analytical methods) is assessed. Case studies are presented to illustrate the use of reactivity monitoring and the types of information that can be obtained. Other more involved and expensive methods are described.

Keywords

Effect sensor, reactivity monitoring, environment, linear cyclic voltammetry.

Research aims

The aim of this work is to review the use of effect sensors to assess environments for metal artefacts. The advantages and drawbacks for different effect sensors for different situations will be assessed.

Introduction

Metals corrode due to the combined effects of a number of environmental factors. The factors that are relevant indoors, depending on the metal are: temperature (including infra-red heating from sunlight, lighting etc), relative humidity, condensation, the concentrations of sulfur dioxide, nitrogen dioxide, nitric acid, ozone, hydrogen sulfide, carbonyl sulfide, hydrogen chloride, chlorine, ethanoic acid, methanoic acid, methanal, alkyl ethanoates, alkyl methanoates, styrene and others, the deposition rate of dust and the chloride, and nitrate and sulfate deposition rate from that dust. Many heritage sites do not have well-controlled environments and these factors can vary widely throughout the seasons.

It is possible to measure all the factors involved (only certain gases are known to affect certain metals) but the large number of factors can make this an expensive task. Often each showcase environment will need to be measured. Even if all relevant measurements are available, only a very limited amount of information has been published to interpret the parameters measured and there are critical knowledge gaps for the interpretation for some metals (Thickett & Lankester, 2012).

Effect sensors have been used for a number of years in conservation (Knight, 1990; Eremin, 1998; Thickett, 2008a). An effect sensor is a piece of material that is exposed to an atmosphere and the effect of that atmosphere on the material is measured. The term dosimeter has been used by several authors; however in many instances the materials react not only to doses of pollutants but also to RH (relative humidity) levels and many other factors. Effect sensors are a convenient way of assessing and comparing environments. This work describes and assesses their use in a number of different situations that require differing levels of analysis and interpretation.

Metal effect sensors

For metals, metal coupons are an obvious choice for assessing how an environment affects a metal. The metal coupon integrates the effects of the environment on the metal by being subject to corrosion. The corrosion is analysed to quantify those effects. The amount of corrosion produced on an object in a given environment will depend on the details of the object; principally its composition, metallurgy and surface finish. Use can affect an object's corrosion, with wear changing surface properties, contamination of the surface, potential and potential changes to metallurgy. Burial often fundamentally changes the nature of archaeological metals and they can react very differently when compared to identical objects kept out of the ground. Some conservation treatments affect the way that objects interact with their environment (intentionally or not). Many copper cleaning treatments from before the 1970s included sodium hydroxide; the inclusion of sodium hydroxide caused mixed sodium copper corrosion products in environments containing carboxylic acids (Thickett, 1998; Trentelman *et al*, 2002). Silver cleaning with silver dips based on acidified thiourea leave a very thin layer of thiourea chemically bonded to the silver surface; this can affect subsequent tarnishing. Additionally, many silver polishing cloths contain tarnish inhibitor additives (Goddards, 2013). The response of a metal coupon will therefore be an indication of the effect on a metal object and not an exact measure unless significant work is done to make the coupon more representative of the particular object. Figure 1 shows a representation of this process.

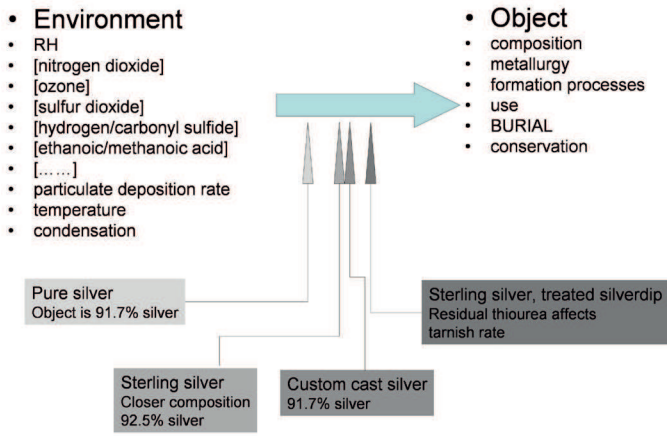

Figure 1: The environmental factors are listed on the left and the object parameters on the right. Burial is in capitals as it has an extremely large effect on many metals response to the environment. The environment affects the object, shown by the thick blue arrow. A series of effect sensors could be produced. The effect sensor responses become more representative of the object in question as it is modified to be more similar, moving left to right. The example shown is for silver coupons used to assess the environment around a 19th century centre-piece. Schematic of use of metal coupon

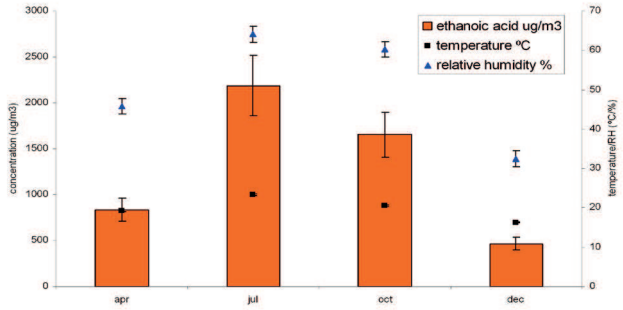

Figure 2: Ethanoic acid concentration in showcase measured in different seasons

Deploying metal coupons

Metals are readily available in a variety of compositions and coupons are relatively inexpensive and can be deployed in large numbers. Surface preparation is extremely important and can affect the results. It is best to follow the standard ISO9223 (EN ISO 2012).

If an environment is variable (not air conditioned) then the time and season of exposure is important and will affect the results. In the UK in the late autumn the environment in most buildings has comparatively high temperature and relative humidity. There are strong seasonal differences in ozone and hydrogen sulfide and other gases in some areas. The emission from woods of ethanoic (acetic) and methanoic (formic) acid increases with increasing temperature and relative humidity. Coupled with the seasonality of these parameters this means that in many buildings the concentration of these gases varies widely inside enclosures containing wood products. Figure 2 shows the ethanoic acid concentration inside a series of showcases throughout the year. The ethanoic acid concentration was measured with diffusion tubes (Gibson *et al*, 1997). The results are averages of four diffusion tubes for each measurement. Temperature and relative humidity were measured with Hanwell radiotelemetry sensors (temperature $\pm$ 0.1 ºC, RH $\pm$ 3%, three point calibration)

The ethanoic acid concentration changes by a factor of three. Other research has reported seasonal differences of a factor of ten (Grontoft, 2012). The ideal scenario is to deploy coupons for multiples of a year to capture the seasonal effects.

Diffusion and colourimetric based measurements and indicators are available to measure gas concentrations (Gibson *et al,* 1997; Tétreault, 1992; Hackney, 2013; Tompkins & Goldsmith, 1977). These generally respond or are deployed for between 1 and 28 days. Multiple measurements are required to assess the environment over a year. Four separate 28 day diffusion measurements have been shown to be representative for some gases if spread seasonally (Thickett *et al* 2013).

Analysing metal coupons

Analysing the coupons after exposure can be by simple inspection or by use of a variety of instrumental analytical techniques.

Inspection by eye can accurately rank coupons; this has been the *de facto* standard for objects, as problems will often only be identified when observed by a conservator inspecting the collection. A systematic approach is required if small differences are to be differentiated and for objective results. Several industrial standards exist that could be readily modified to achieve this (ASTM, 2005; ASTM, 2010). A method similar to that devised to assess dust deposition could be used (Lloyd *et al,* 2011) Image analysis has been reported for silver and copper coupons (Wang *et al,* 2011) and colourimetry has been suggested to analyse silver and lead coupons (Thickett, 2008A; Tétreault *et al,* 1998).

Colourimeters often analyse a circular area of area generally less than that of the whole surface; some coupons corrode preferentially at the edges, which can be problematic for this approach. It is also important not to contaminate the silver surface if marking an area to repeat colourimetry after exposure, as this can affect the tarnish rate. The decision to clean a silver object is generally based on aesthetic response, often by a curator, and colourimetry can

determine this well. If a survey of decision makers is carried out to determine the point at which cleaning is required and the apparent tarnish rate is determined by colourimetry then lifetime predictions for cleaning are possible. The surface of lead corrodes by initially becoming darker and then lighter; this can cause an issue with colourimetry as the same reading can occur during the darkening and then again after the lightening as hydrocerrusite forms.

Mass gain is an easy way to assess coupons but can give misleading results. Different corrosion products have different molecular masses so the same mass gain on two coupons with different corrosion products will be caused by the loss of different amounts of metal. For this reason standards to strip the corrosion product to determine the amount of metal lost through corrosion and results are usually quoted as a loss of metal per unit area per year. Chemical and electrochemical methods for stripping corrosion to determine the mass loss for a range of metals are given in ISO9223 (EN ISO, 2012) and ISO11844-1 (EN ISO, 2008). All of the chemical agents, some of which have safety implications, also slowly dissolve the metal. Therefore, multiple immersions are required and a calculation is undertaken to correct for the additional metal dissolved along with corrosion products on the first immersion.

Figure 3 shows results from a mild steel coupon. This is one of a set of three exposed for a year in the secret wartime tunnels under Dover Castle to assess the relative corrosion rates and impact of dust on that corrosion (Thickett, 2008B). The initial mass was 155.67 mg for the 1.5 by 2 cm coupon. The coupon was polished with 1200 grade silicon carbide paper then immersed in propanol and dried over silica gel. The mild steel composition was selected to match the composition of steel communications equipment and racking that had been analysed with portable X-ray fluorescence. In Figure 3, multiple immersions (500 ml hydrochloric acid (spg 1.19, 3.5 g hexamethylene tetraamine, made up to 1000 ml) were undertaken and a linear regression applied to determine the correct mass of the coupon minus the corrosion products as being 153.22 mg.

Care needs to be taken on drying the coupons after stripping, as flash corrosion is common. A chamber with dry silica gel was used to ameliorate this risk.

The major drawback with chemical stripping is that all information about the nature of the corrosion products is lost; this information can be useful in identifying the source of the corrosion (Thickett and Odlyha, 2003; Thickett and Pretzel, 2010). Analysis can be undertaken before stripping if available. Some electrochemical techniques such as linear sweep voltammetry (LSV) can provide information about the corrosion products that are present (from the peak positions) whilst determining the amount of metal stripped from the corrosion (from the peak areas) (Costa and Dubus, 2007). To date, this method has only been developed for silver and copper corrosion. The method is also useful to analyse coupons that were not weighed before exposure, which is a requirement for chemical stripping.

At Rangers House in London, lead coupons (2 cm by 1.5 cm, cleaned with 1200 grade wet and dry paper and then immersion in propanol, dried above silica gel before weighing, taking appropriate precautions for dealing with hazardous lead) were exposed in eleven showcases to assess the risk from inadequately sealed medium density fibreboard (MDF) boards. The boards had been sealed with the acrylic lacquer, Dacrylate 109, a product known to provide a good barrier against methanal (formaldehyde) but almost no barrier against ethanoic and methanoic acid, emitted from all MDF (Thickett, 1998). Two sets of eleven coupons (one per case) were deployed in 2004. One set was analysed after six months in October to provide an initial assessment of the worst (late summer and autumn) period. A second set was analysed after three full years for a better overall picture. The coupons were analysed with X-ray diffraction (Phillips diffractometer with Cu radiation and 40 mV and 40 mA and Fourier transform infra-red spectroscopy (Perkin Elmer, 2000, with Amplif-IR accessory) before stripping for five minutes with 250 g/l ammonium acetate at 60 °C. Results are shown in Figure 4.

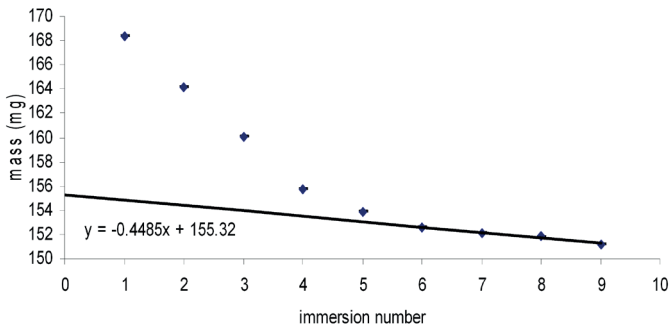

Figure 3: Stripping of iron coupon exposed for twelve months. Errors are determined from balance accuracy.

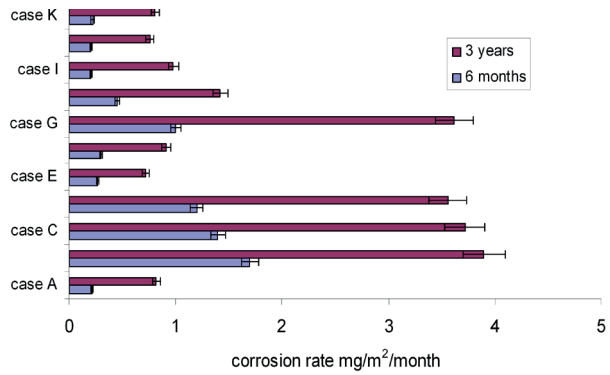

Figure 4: Lead corrosion in a series of showcases. Errors are determined from balance accuracy.

The coupons had low corrosion rates. The preliminary proposed lead standard for pure air is <3 nm/30 days (Proseq *et al,* 2013); therefore, taking the density of lead to be 11.34 g/cm^3 this gives a metal loss of slightly over 34 mg/m^2/30 days. There were differences between the showcases, which have been assigned to differing air exchange rates (Thickett *et al,* 2006).

The coupons all had plumbonacrite, $6PbCO_3.3Pb(OH)_2$. PbO, and mixtures of lead oxides (α-PbO, β-PbO, and PbO_2) and oxide hydroxide $3PbO.H_2O$ on their surfaces.

The initial corrosion rate is much higher, with the amount of corrosion at three years being much less than three times the corrosion rate at six months. No corrosion was visible to the naked eye. Later ethanoic acid measurements by diffusion tubes (Gibson *et al,* 1997) indicated autumn concentrations of between 330 and 650 µg/m^3. This falls within the bottom quartile of the 600 or so measurements undertaken by the author.

An advantage of this method is that it can be used for very long term monitoring of environments.

Monitoring corrosion long term

Similar experiments in a series of 13 showcases in the British Museum analysed lead coupons after ten years of exposure, with X-ray diffraction (XRD) before stripping (the AmplifIR accessory was not available at that time). Ethanoic acid concentrations were measured with diffusion tubes, with a 30 day measurement in each season and eight measurements taken over a two year period in each showcase. Results from the stripping and the minimum, maximum and interquartile ranges of the eight ethanoic acid measurements for each showcase are shown in Figure 5.

The dark purple bars (cases a through j) had plumbonacrite and the same lead oxide corrosion products on the surface as previously and had no visible corrosion present. The paler purple bars (cases k, l and m) had visible white corrosion that was analysed as hydrocerussite, $2PbCO_3.Pb(OH)_2$, by XRD. These results and the results from Rangers House indicate that lead can withstand a somewhat higher concentration of ethanoic acid than the 100 µg/m^3 limit proposed by Tétreault *et al* (1998). The lead coupons exposed for ten years had measurements between 87 and 430 µg/m^3 and the majority of the exposures that were much greater than 100 µg/m^3 had no visible corrosion or hydrocerrusite present on their surfaces. The RH measured in the showcases over the ten year period ranged from 30 to 79%, with the higher RHs corresponding with the highest ethanoic acid concentrations.

The tarnish layers that form on silver are disfiguring even though they are often very thin; surface sensitive techniques are required to identify or quantify them. Table 1 details the techniques reported for this purpose. The information depth is important and can lead to different results between techniques. Image analysis (Wang *et al,* 2008) has only been applied to coupons exposed to artificial atmospheres and not for environmental monitoring even though it could be readily applied for this application.

Development of effect sensors

The MEMORI project is integrates two effect sensors to produce a general sensor suitable for use in enclosures (MEMORI, 2013). The glass slide dosimeter is responsive to RH and ethanoic and methanoic acids, and its response is measured in the infra-red range (Grøntoft *et al,* 2010). The polymer early warning organic sensor is sensitive towards nitrogen dioxide, ozone, ultraviolet and RH, and its response is measured in the UV range (Grøntoft *et al,* 2010). The project is developing a portable reader that can accurately measure the response of the effect sensors. The project's web pages will collate the response with published reactivity data for metals important in cultural heritage.

Effect sensors are normally deployed for a minimum of four weeks and often longer. There are situations when more immediate results are required. Some of the more advanced analytical techniques, SIMS [secondary ion mass spectrometry], XPS [x-ray photoelectron spectroscopy], LVS are sensitive and can measure changes to metal coupon surfaces in under four weeks in aggressive environments. There are two technologies that have been developed to have very high sensitivity: quartz microcrystal balances and resistivity based sensors. Quartz crystal microbalances resonate at a very well defined frequency (6 MHz quartz crystal microbalances are available commercially with metal coatings). When coated with a metal, this resonant frequency drops. Further increases in mass (as the metal corrodes) reduce the resonant frequency further. Resistivity based sensors consist of two thin metal tracks. One of the metal tracks is coated with a lacquer to prevent corrosion. As the other track corrodes, the depth of metal decreases and its resistivity increases. The effect is very temperature dependant and the resistivity of the reference (lacquer coated) track is measured to compensate. These methods give a direct measurement of corrosion rate, require no further analysis and are available as continuous loggers. Having continuous data can be extremely useful as it can be correlated with other continuous monitoring such as temperature, RH, condensation (Montross *et al,* 2006) or with the operational activities on a site, for example when doors and windows are open, the operation of ventilation and air conditioning systems, visitor numbers and cleaning operations.

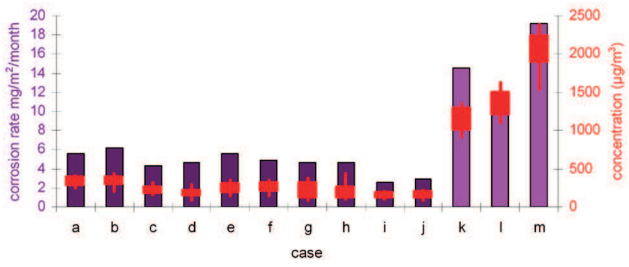

Figure 5: Long term lead corrosion rates in a series of showcases at the British Museum. Dark purple bars lead coupons with no visible corrosion, pale purple bars, coupons with visible corrosion, red boxes interquartile ranges of ethanoic acid concentration, lines full ranges of ethanoic acid concentration. Error bars have not been included in the corrosion rate bars as they are extremely small due to the balance accuracy and very long term exposure.

Quartz microcrystal balances coated with a variety of metals have been produced. Silver and copper coated 6 MHz crystals are available commercially from Purafil along with a logger to read them. Other metals can be used, such as lead and higher frequency crystals, to increase sensitivity and reduce the effect of dust deposition on the measurements (Odlyha *et al,* 2010). The 6 MHz crystals are affected by dust deposition and the commercial system has a perspex cover to minimise this; the manufacturers recommend that the units are deployed with the flat crystal surfaces pointing down. Dust can have an effect on the corrosion of several metals (Vernon, 1935) and excluding this effect will not provide a representative measure of some atmospheres. The effect of increased mass through dust deposition cannot be separated from the increase in mass through corrosion caused by that dust.

Results from Onguard silver crystal exposures in two rooms with different conditioning systems at Apsley House in central London are shown in Figure 6.

The difference between the two room environments, one with chemical filtration, the other without, can be clearly seen within a day. Longer term results are shown in Figure 7.

Changes in the rate of corrosion are clearly visible on the traces. This data has been correlated with temperature, RH, nitrogen dioxide, sulfur dioxide and ozone data to produce indoor damage functions for copper and silver (Thickett *et al,* 2013)

A resistivity based sensor and logger has been commercialised through the EU project MUSECORR (MUSECORR, 2013). A variety of metals and sensitivities (the depth of the metal grid) are available. The sensor will determine the affects of dust on corrosion of the metal grid used. A series of silver, copper, lead and iron sensors were tested on English Heritage sites (along with several other institutions) as part of the project. Results have not been included here due to space limitations.

Conclusions

A variety of methods are available to measure atmospheric pollutant gases. However interpreting these results is not straightforward in many environments and for some metals the baseline data necessary to allow interpretation do not presently exist.

Metal coupons provide a relatively inexpensive way to assess environments for heritage metals. The ability to monitor both very short (a few hours) and very long (several years) term periods allows their use in a number of situations. The long term monitoring results presented here indicate that the present standards for monitoring lead and ethanoic acid (Tétreault *et al* 1998) are insufficient and that lead can safely withstand somewhat higher concentrations. Analysis can be simply visual or involve a wide range of analytical techniques to gather information about the metal environment interaction from the exposed coupons. They detect synergistic effects that are difficult to assess with other methods.

Analysing metal coupons after exposure can be expensive and time consuming depending on the information desired and this is often the major limitation on their use. The MEMORI system allows for rapid, on-site analysis of its glass and polymer effect sensors. Metal based systems, such as Onguard and MuseCorr, are loggers that measure the response of metals to the environment. This additional high time resolution information can be extremely useful in determining the causal factors for metal corrosion and informing improvements to the environment for better preservation.

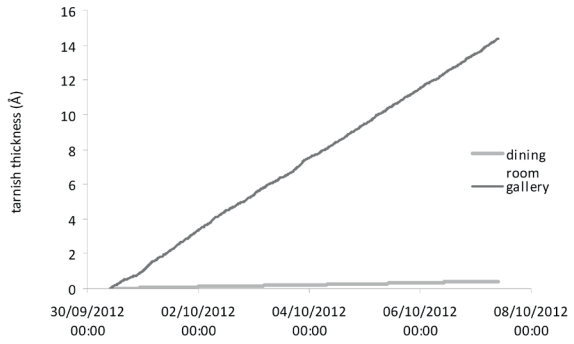

Figure 6: Response of silver coated quartz crystal to two different environments in rooms at Apsley House, central London

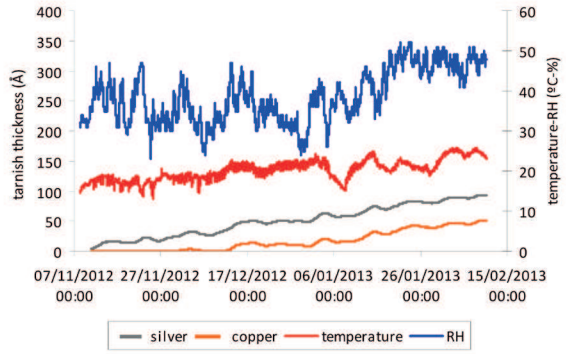

Figure 7: Longer term monitoring with silver and copper coated quartz crystals

	Detects	Information depth	Reference
Colourimetry	b* or Y	Probably whole	Thickett, 2008A; Ankersmit *et al,* 2001
Image analysis	Percentage coverage	Visible depth only, thicker layers will not cause more response	Wang *et al,* 2011
LSV	Sulfide, oxide and chloride	whole	Costa & Dubus, 2007
SEM-EDX	Sulfur, chlorine, oxygen, carbon	~1 µm	
XPS	Sulfide, sulfate, oxide	~ 10 nm	Bradley, 2003
Static SIMS	Species <300 Da	0.3 nm	Hallett *et al,* 2003
Dynamic SIMS	Species <300 Da	whole	Hallett *et al,* 2003
Grazing angle XRD	Sulfide, chloride, oxide	whole	
FTIR	Sulfate	whole	

Table 1: Techniques used to analyse silver coupons.

References

Ankersmit H. A., Doménech Carbó A., Tennent N.H. 2004. Tarnishing of silver: evaluation by colour measurements. In *Proceedings of the International Conference on Metals Conservation: Metal 2001*, *ICOM-CC Metals Working Group and Western Australian Museum, Perth,* , ed. I. D. MacLeod, J.M. Theile and C. Degrigny, pp.157-166. Perth, Australia.

ASTM G46-94, 2005. *Standard Guide for Examination and Evaluation of Pitting Corrosion, Active Standard ASTM G46* Developed by Subcommittee: G01.05 |Book of Standards Volume: 03.02 West Conshohocken: American Society for Testing and Materials.

ASTM G33-99., 2010. *Standard practice for recording data from atmospheric corrosion tests of metallic-coated steel specimens*. West Conshohocken: American Society for Testing and Materials.

Bradley S., 2003. Preventive conservation: the research legacy. In *Conservation Science 2002, 22-24 May 2002,* pp.3-7. Edinburgh, Scotland: Archetype Publications.

Costa V., Dubois M. 2007. Impact of the environmental conditions on the conservation of metal artifacts in *Museum Microclimates, 2007, Copenhagen* ed T.Padfield and K. Borchersen, pp. 63-65, Copenhagen: National Museum of Denmark.

EN ISO 9223, 2012.. *Corrosion of metals and alloys - Corrosivity of atmospheres -Classification, determination and estimation*, ISO Geneva

EN ISO 11844-1 2008. *Corrosion of metals and alloys. Classification of low corrosivity of indoor atmospheres*. ISO Geneva

Eremin K., Wilthew P., 1998 Monitoring concentrations of organic gases within the National Museums of Scotland, *Scottish Society of Conservation and Restoration Journal*, 9(1), pp.15-19.

Gibson L., Cooksey B.G., Littlejohn D., Tennent N.H., 1997 A diffusion tube sampler for the determination of acetic acid and formic acid vapours in museum cabinets. *Analytica Chimica Acta*, 341, 1, pp.11-19.

Goddards Ltd, 2013 personal communication.

Grøntoft T. 2012 Performance evaluation for museum enclosures, measurement, modelling and mitigation of pollutant impact on objects in museum enclosures. *E-Preservation Science* 9, pp.36-46.

Grøntoft T., Odlyha M., Mottner P., Dahlin E., Lopez-Aparicio S., Jakiela S., Scharff M., Andrade G., Obarzanowski M., Ryhl-Svendsen M., Thickett D., Hackney S., Wadum J. 2010. Pollution monitoring by dosimetry and passive diffusion sampling for evaluation of environmental conditions for paintings in microclimate frames. *Journal of Cultural Heritage* 11, pp.411-419.

Hackney S. 2013 personal communication

Hallett K., Thickett D., Chater R., McPhail D. 2003 Application of SIMS to silver tarnish at the British Museum. *Applied Surface Science* 203-204, pp.789–792.

Knight B. 1994. Passive monitoring for museum showcase pollutants, In Preventive conservation: practice, theory and research. In *Preprints of the contributions to the Ottawa Congress, 12-16 September 1994,* A. Roy and P. Smith, pp.174-176. Ottawa, Canada: International Institute for Conservation of Historic and Artistic Works.

Lloyd H., Grossi C.M., Brimblecombe P. 2011, Low technology dust monitoring for historic collections. *Journal of the Institute of Conservation*, 34 (1), pp.106-116.

MEMORI EU-Research Project: Measurement, Effect Assessment and Mitigation of Pollutant Impact on Movable Cultural Assets. Innovative Research for Market Transfer. European Commission, [viewed 25 March 2013]. Available from: http://www.memori-project.eu/memori_project.html

Motross M.D., Duncan G.A., Gates, R.S. 2006. Development and testing of a low cost condensation detection system,. *Applied Engineering in Agriculture* 22(4), 602-608.

MUSECORR: Protection of cultural heritage by real-time corrosion monitoring. European Commission, [viewed 25 March 2013]. Available from: http://www.musecorr.eu/

Odlyha M., Jakiela S., Bergsten C.J., Slater J., Niklasson A., Svensson JE., Cavicchioli A., de Faria D.A, Thickett D., Grøntoft T., Dahlin E. 2010.Dosimetry for monitoring in organ pipes and in microclimate frames for paintings. In *Proceedings of Metal 2010, 11-15 October 2010, Charleston*, ed. P. Mardikian, C. Chemello and P. Hull, pp.321-326.

Prosek T., Kouril M., Dubus M., Taube M., Hubert V., Scheffel B. Degres Y., Jouannic M., Thierry D. 2013. Real-time monitoring of indoor air corrosivity in cultural heritage institutions with metallic electrical resistance sensors. *Studies in Conservation*, 58(2), pp.17-128.

Tétreault J., Sirois J., Stamatopoulou E. 1998. Studies of lead corrosion in acetic acid environments. *Studies in Conservation,* 43(1), pp.17-32.

Tétreault J. 1992 La mesure de l'acidité des produits volatils. *Journal of IIc-CG* 17, 17-25.

Thickett D. 1998 Sealing of MDF to prevent corrosive emissions. *The Conservator,* 22, pp.49-56.

Thickett D., Odlyha M. 2000. Note on the identification of an unusual pale blue corrosion product from Egyptian copper alloy artifacts. *Studies in Conservation,* 45(1), pp.63-67.

Thickett D., David F., Luxford N. 2005. Air exchange rate: the dominant parameter for preventive conservation. *The Conservator,* 29, pp.19-34.

Thickett D., 2008A. Presentation in situ through microclimates. In *Contributions to the Congress: Conservation and Access, The International Institute for Conservation of Historic and Artistic Works, 15th-19th September 2008, London,* ed. D. Saunders, J.H. Townsend and S.Woodcock, pp.98-103.

Thickett D. 2008B. *Investigation into the role of inert dusts in corrosion and corrosion mitigation in an aggressive maritime environment*, *Ligas Metalicas* Universidade de Porto, pp.75-89.

Thickett D., Pretzel B., 2010 Micro-spectroscopy: a powerful tool to understand deterioration. *E-Preservation Science*, 7, pp.158-164.

Thickett D., Lankester P. 2012 Critical knowledge gaps in environmental risk assessment and prioritizing research. *Collections*, 8(4), pp.281-296.

Thickett D., Chisholm R., Lankester P., 2013. Development of damage functions for copper, silver and enamels on copper. In *Climate for collections, standards and uncertainties, 7-9 November 2013, Munich* ed. J. Ashley-Smith, A. Burmester and M. Eibl, available at http://www.doernerinstitut.de/downloads/Climate_for_Collections.pdf accessed July 2013

Tompkins F.F., Goldsmith R.L., 1977. A new personal dosimeter for the monitoring of industrial pollutants. *Journal American Industrial Hygene Association* 38, pp.371.

Weber W.H., Chen A., Garrett S.J., 2002. The characterization of a new pale blue corrosion product found on copper alloy artifacts. *Studies in Conservation* 47(4), pp.217-227.

Vernon W. H. J., 1935. A laboratory study of the atmospheric corrosion of metals: Part II, iron: the primary oxide film; Part III, the secondary product or rust (influence of sulphur dioxide, carbon dioxide, and suspended particles on the rusting of iron). *Transactions of the Faraday Society,* 31, pp.1668-1700.

Wang S., An Z., Chen J., Kong L., Wu L., Zhuou X., 2011. An improved oddy test using metal films. *Studies in Conservation,* 56, pp.138-153.