

Real-time monitoring of indoor air corrosivity in cultural heritage institutions with metallic electrical resistance sensors

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Abstract

A system for continuous monitoring of atmospheric corrosivity has been developed. An electronic unit measures and records changes in the electrical resistance of a thin metal track applied on an insulating substrate. If the metal corrodes, the effective cross-sectional area of the track decreases and the electrical resistance increases. Sensors made of silver, copper, iron/steel, zinc, lead, tin, aluminium, bronze and brass at thicknesses from 50 nm to 250 µm were tailored for environments with different corrosivities. The developed technology proved capable of providing high sensitivity, allowing for real-time corrosion monitoring even in low-corrosive indoor cultural heritage facilities. Laboratory tests showed good reproducibility with the standard deviation of parallel measurements at less than $\pm 20\%$ for metals which corrode uniformly in the tested environments. Several examples selected from a broad testing programme in partner museums, libraries and other institutions show successful applications of the logger system for characterisation of air quality control in indoor locations, during transport and in temporary exhibitions; assessment of new buildings and storage facilities; and fundamental studies of optimal conservation and storage procedures. A first outline of a classification system for lead, which is particularly sensitive to the presence of carboxylic acids, is given. The technique has a large potential as an independent method for monitoring air quality in facilities displaying and storing valuable objects of cultural heritage.

Keywords: Air quality control; Metal corrosion; Material degradation; Reactive monitoring; Copper; Silver

Introduction [heading]

A great number of both movable and stationary cultural assets are managed by cultural heritage authorities all over the world. Degradation of culturally-significant objects stored or displayed in indoor premises is

affected by air temperature, relative humidity, concentration of pollutants such as sulphur dioxide, nitrogen oxides, ozone, ammonia, hydrochloric acid, sulphates, dispersed chlorides, organic acids, other volatile compounds and dust particles. Although the deterioration of objects due to the presence of indoor pollutants is often slow, its cumulative effect is largely surpassing much more spectacular damages caused by fires, theft, earthquakes, flooding etc. combined.

Due to a high number of possible indoor pollutants and their interactions and costs and technical problems associated with monitoring them, it is only the relative humidity and temperature that are controlled and monitored by most institutions. Air filters, scavengers and other additional anti-corrosion measures are applied only to protect most valuable collections or when valuable and often-irreplaceable historical objects have already been affected. Any air quality control scheme without application of a monitoring technique giving rapid feedback on the air quality might be either inadequate or excessive, and thus too costly. Thus, information on the actual corrosivity of the atmosphere is crucial to the effective corrosion protection.

Direct impact of atmospheres on objects is traditionally followed by exposing coupons of given materials to the environment and consequent analysis of their degradation after given period of time. For non-metallic materials, the coupon technique is rarely used, but projects on development of specific coupons or dosimeters are in progress [1]. In contrary, it is well established for metallic materials. According to current standards, a metal coupon needs to be exposed for 30 days or for 1 year in given environment. The impact of the environment on metal degradation is evaluated in a specialized laboratory based on mass loss, mass gain or coulometric reduction of corrosion products. The mass loss procedure is used for an assessment of outdoor corrosivity whereas the mass gain is measured usually on coupons exposed indoors. The coulometric reduction of corrosion products is more demanding with respect to equipment and experience, but can provide an indication of the nature of the pollution in addition to the rate of metal degradation.

However, none of the coupon techniques can be considered as real-time. Within the exposure period, valuable objects might further deteriorate if the air is contaminated. Thus, there is a strong need for a tool enabling cultural heritage professionals to assess the air corrosivity in real time. Because open-air museums, artefacts of industrial activities, and even entire factories are presently recognized as important parts of cultural heritage, the need for atmospheric corrosion monitoring is not limited to indoor conditions with air quality control but must also be available for outdoor environments.

Whereas there is a relatively wide range of products for corrosion monitoring in aqueous media, the availability of means for real-time corrosion monitoring in the atmosphere is limited. Thus, an electronic logger enabling a continuous measurement of the corrosion rate of selected metals in air has been developed.

The electrical resistance (ER) technique was selected to measure the corrosion rate within projects supported by the European Commission [2,3]. The technique is described in, e.g., ASTM standard G96 [4]. The principle of the method is that the electrical resistance of a measuring element made of the material of interest increases as its effective cross-sectional area decreases due to corrosion. In practice, two such elements are built into a probe. One element is exposed to the corrosive environment and corrodes, whereas

the other element is shielded and, thus, protected from corrosion. The resistances of both elements are measured at the same time and resistivity changes due to varying temperature are compensated for. Based on the initial cross-sectional area of the exposed element, the cumulative metal loss at the time of reading can be determined. The benefits of the ER technique include its versatile nature as it can be used in practically any kind of environment, robustness and ability to provide continuous measurements [5,6].

This paper provides a description of the technique, results of laboratory tests on its reproducibility, sensitivity and accuracy and several examples of applications in cultural heritage institutions.

Corrosion monitoring system [heading]

The monitoring system is comprised of four principal parts: an electronic logger for measuring and recording ER, a metal sensor that actually corrodes in the environment, a communication interface between the logger and computer and a software programme for interpretation of the measurement.

The concept of the measuring device is simple and yet highly effective: the electronic unit measures and registers the change over time of the electrical resistance of a thin metal track applied on an insulating substrate. A schematic drawing of the sensor is shown in Figure 1. The width of the measuring track is from 1 to 2 mm, depending on sensor type, and the length is over 100 mm. This geometry ensures high sensitivity to changes in the electrical resistance due to metal corrosion.

In contrast to traditional designs [7], the sensing and reference parts of AirCorr sensors are connected by an H-shaped bridge. The edge of the protective coating passes approximately through the middle of the bridge. Thus, the edge of the protective coating is neither part of the sensing nor of the reference track and the bridge serves only as a conductor for passage of the testing current. The measuring part of the track is placed a safe distance from the coating edge. This design solves a common problem of ER probes, which is corrosion of the metallic track at the interface between the sensing and reference parts underneath the protective coating, which can lead to erroneous readings [10]. A patent application has been filed to protect this unique solution.

The sensitivity and service life of the sensors depend on the thickness of the metallic track: the lower the thickness, the higher the sensitivity. On the other hand, low thickness leads to a shorter service life. The service life can be assessed as the time to consume one half of the track thickness. Therefore, sensors with different track thicknesses are available for applications in different environments.

Assuming that the electrical conductivity of the track is proportional to the remaining metal track thickness and assuming that corrosion products do not contribute to the conductivity, the corrosion depth of the metallic sensor, Δh , can be calculated according to equation

$$\Delta h = h_{ref,init} \left(\frac{R_{ref,init}}{R_{sens,init}} - \frac{R_{ref}}{R_{sens}} \right) \quad (1)$$

where $h_{ref,init}$ is the initial thickness of the reference metallic track, which is considered to be equal to the sensing track at the beginning of exposure, R_{sens} and R_{ref} are the resistances of the sensor and reference tracks at the time of measurement, and $R_{sens,init}$ and $R_{ref,init}$ are the initial resistances of the sensor and reference tracks [8–10]. The calculation is based on the electrical resistances measured as a potential difference along the track through which defined currents pass. The equation has been improved compared to the earlier one in order to be valid throughout the whole service life of the sensor [5].

For indoor use, the protection of the reference track against corrosion is provided by an organic adhesive tape coated with an inorganic diffusion barrier layer. The coating is transparent to avoid differential heating of the tracks.

Sensor materials and thicknesses are listed in Table 1. Photographs of several types of thin- and thick-film sensors are shown in Figure 2.

The changes in electrical resistance are recorded by precise electronic loggers. Three versions of AirCorr loggers were developed for specific applications as seen in Figure 3. The basic versions of the electronic logger, I and O, are encased within a small watertight polycarbonate box measuring 100×65×37 mm with a tightness of IP 65. For the indoor version, I, the logger lid is provided with a connector so the sensor can be easily replaced when necessary. Version O for outdoor applications in highly corrosive environments has an attached sensor protected with a robust polyurethane casting. The lid can be replaced when the sensor is at the end of its useful life. The devices are equipped with an LED that signals when the unit is on. Version I Plus is also designed for indoor use and can measure the air corrosivity on two sensors of identical or different metals. In addition, temperature and relative humidity are registered. Current corrosivity and climatic parameters can be read on a build-in LCD display. The cadence of the measurement can be adjusted from minutes, to hours, to even days if necessary in order to match the sensitivity of the measurement with the anticipated corrosion rate.

Collected and stored data can be downloaded by a non-contact inductive data reader, even through showcase glass. A GPRS/GSM access unit is optional and allows remote data access and control with automatic data delivery via e-mail. The loggers are designed to be autonomous for five years. The battery itself is also replaceable. The loggers are fully independent of any power supply, any external control, and can, therefore, be placed anywhere. User-friendly software allowing for rapid interpretation of results and incorporating existing and proposed standards and recommendations has been developed. Further information is available elsewhere [11].

Laboratory testing [heading]

Sensitivity of measurement [sub-heading]

The sensitivity of the thin film sensors developed for lightly-polluted indoor locations was tested in air during a cycle comprising changes in relative humidity from 30 to 85% and changes in temperature from 20

to 30 °C. An example of such measurement is given for a copper sensor with the metal track thickness of 500 nm in Figure 4. The sensor was initially exposed to air at ambient temperature and a low relative humidity of about 33%. It was then transferred to a climatic chamber with controlled temperature and relative humidity of 20 °C and 85 %. Finally, the temperature was increased to 30 °C. As seen in Figure 4a, the changes in the air corrosivity were observable within several minutes. Figure 4b shows extrapolated curves indicating that the corrosion rate of copper increased from 0.3 nm/month (3 nm/year) in dry air to 2 nm/month (24 nm/year) in humid air at 20 °C and further to 7 nm/month (85 nm/year) at the elevated temperature of 30 °C. The rates correspond to corrosivity classifications of IC 1 – Very low, IC 2 – Low and IC 3 – Medium, respectively, according to ISO 11844-1 [12]. The standard requires 1-year exposure in a given environment to establish the classification and the obtained data are thus only indicative. Anyway, the experiment demonstrates the extreme sensitivity of the technique and the ability to assess the air corrosivity within only several hours.

The corrosion depth Δh can be recalculated to corrosion build-up b (thickness of the layer of corrosion products) using equation

$$b = \frac{\rho_M \cdot c \cdot \Delta h}{\rho_{CP}} \quad (2)$$

where ρ_M is density of metal (8.9 g cm⁻³ for copper), c is a ratio between the mass of formed corrosion products and the mass of corroded metal (1.5 for copper [12]) and ρ_{CP} is density of the corrosion products (6.0 g cm⁻³ for cuprous oxide, Cu₂O [13]). Details on the formula construction and its limitations are given elsewhere [14]. The corrosivity can be classified based on the corrosion build-up under all conditions as G1-level – Mild using ANSI/ISA-71.04-1985 [15]. According to the corrosivity classification of indoor atmospheres developed by Sacchi and Muller in particular for museums and archives, the two former environments can be classified as S1, Extremely pure and the last one as S2, Pure [16].

A logger with Ag-50nm sensor was exposed to a climatic chamber with air maintained at constant temperature of 25 °C and cycling relative humidity. It started at 80% RH, then dropped to 40% and increased again to 60% and 80% RH. Two such cycles were carried out each day. Records of RH and corrosion depth are plotted in Figure 5. At 40% RH, the corrosion rate was negligible. Corrosion rates of about 50 and 130 nm/year were recorded at 60% and 80% RH, which corresponds to IC 2 – Low and IC 3 – Medium classifications by ISO 11844-1 [12]. The Sacchi and Muller classification system marks the respective environments as S2, Pure and S3, Clean [16]. The recording shows good reproducibility of the sensor response in multiple cycles.

The sensitivity of the measuring device with regard to corrosion may be defined as the minimum mass of corroded metal required for a reliable response of the ER measurement. For a metal film with constant thickness, the extent of corrosion can be represented as a corrosion depth assuming a homogeneous decrease of metal thickness. Such calculated corrosion depth is a mean value based on simplified model assumptions. Seemingly very small changes in corrosion depth values at sub-Ångström (<10⁻¹⁰ m) level can be calculated

using equation (1), but these do not have a direct physical meaning. Such changes can instead be associated with oxidation of a portion of an atomic layer. Localised corrosion, e.g. at grain boundaries, would obviously strongly influence the ER of a thin metallic track. Nevertheless, the simple model has proven to be successful.

This sensitivity was at least 1/1000 of the initial metal track thickness varying from below 0.1 nm ($<10^{-10}$ m, $<1 \text{ \AA}$) for sensors developed for low-corrosive indoor environments to 200 nm for the robust 250- μm steel sensor designed for highly corrosive outdoor applications. The sub-Ångström sensitivity of the thin-film sensors is very apparent in the recordings shown in Figure 4a and in Figure 5.

Reproducibility and accuracy of measurement [sub-heading]

A series of experiments were performed in air with controlled temperature, relative humidity and concentrations of carboxylic acids. Formic acid and acetic acid were released to feed air at concentrations from several tens to close to 3000 ppb. The experiments were partly reported previously [10,8,9] and a paper with further results has been submitted for publication [17]. In each experiment, three parallel loggers with identical sensors were exposed to assess the measurement reproducibility. The measured corrosion depths with standard deviations are shown in Figure 6. With exception of the Fe-800nm sensors in air with formic acid, the reproducibility was better than $\pm 20\%$. The large scatter for parallel Fe-800nm sensors was due to non-uniform corrosion.

Because of the high sensitivity of the setup, it was not possible to compare the results to those obtained using traditional techniques following measurements in low-corrosive atmospheres. To get an idea of the accuracy of the technique, thick-film sensors for outdoor applications were tested in two accelerated tests. The ECC1 test according to Renault standard D17 2028/2002 is a cyclic wet/dry test performed at a constant temperature of 35 °C and comprises spraying the samples with a solution of 1 wt. % NaCl at pH 4 for 30 minutes each day. The second test, which follows the EN ISO 3231 standard is run at 40 °C and at 100 % RH in air with 500 ml of SO₂ generated in a 300-litre chamber. Selected sensors were exposed to the tests together with corresponding metal coupons. At the end of the exposure, the weight loss of the coupons was evaluated following ISO 8407. The weight loss results were re-calculated to corrosion depths assuming that the corrosion was uniform. As seen in Figure 7, the reproducibility was even higher than for the thin-film sensors and good correlation between the corrosion depths measured by the electrical resistance sensors and the metal coupons was obtained in most cases. The Cu-9 μm sensors gave significantly higher corrosion depths than the coupons and an improved sensor with a higher thickness, Cu-12 μm , had to be developed as a replacement.

The data usually show somewhat higher corrosion depth for the ER sensors than for metal coupons. This is not surprising since the ER technique gives by its nature the maximal depth of attack, while the coupon technique provides an average corrosion depth. For example, the Zn-50 μm sensor exposed to the SO₂ test showed 2-times higher corrosion depth than the coupons and cross-section examination revealed that it was

due to non-uniformity of the corrosion. In principle, the applicability of the electrical resistance technique is thus limited to conditions where the corrosion of a given material proceeds mostly uniformly. In a lower extent, the readings for the sensors can be also affected by the edge effect, which is practically negligible in the case of metal panels.

Testing in real environments [heading]

Introduction [sub-heading]

In 2011 and 2012, a large end-user testing programme was conducted in order to assess the performance of the AirCorr monitoring system in real environments and to obtain feedback for the last stage of development. Over 25 loggers with multiple sensors were distributed to conservators and other cultural heritage professionals around the world. The following partners participated in the testing programme: Swiss National Museum (Schweizerisches Nationalmuseum); Centre for Research and Restoration of the Museums of France (Centre de Recherche et de Restauration des Musées de France); National Museum of Denmark (Nationalmuseet); English Heritage, UK; Swiss National Library (Schweizerische Nationalbibliothek NB); Museum of Art History (Kunsthistorisches Museum), Austria; Australian War Memorial; St. Fagans: National History Museum, Wales, UK; The Royal Library (Det Kongelige Bibliotek), Denmark; Czech National Archive (Národní archiv), Czech Republic and The Mariners' Museum, USA. The loggers were used to assess old and new storage facilities, to study the effects of supposedly corrosive factors on air corrosivity, in comparative studies of showcases, for ranking of locations and institutions, for problem solving and in fundamental studies on optimal conservation techniques. Several examples of the applications are given below.

Loan of tapestry [sub-heading]

A unique historical tapestry with copper threads from collection of the Louvre Museum was loaned to two galleries in Japan. A logger equipped with a Cu-500nm sensor accompanied it on its journey to monitor the air quality surrounding the tapestry. The recording plotted in Figure 8 reveals that although the relative humidity and temperature were kept close to target levels, the air corrosivity varied with time. Packing, transport to Japan in a crate, exhibition in Gallery 1 and transport to Gallery 2 were associated with only minor corrosion with the cumulative corrosion depth in 3 months reaching 1.8 nm. However, upon opening the transport box and exhibiting the tapestry in Gallery 2, the corrosivity increased significantly. During the 3-month exhibition in Gallery 2, 8.5 nm of copper corroded and the corrosion rate in the first month was 7.6 nm/30 days. Although this still corresponds to IC 2 – Low corrosivity class according to ISO 11844-1 [12], the air quality control was not ideal in Gallery 2. The record shows that aside from higher fluctuation in the relative humidity, a small amount of some pollutant had to be present in the air to accelerate the corrosion rate of copper. In particular, the increase in the corrosion depth starting on 30/06 indicates deterioration of the air quality.

Such information is indeed very valuable for future decisions on loans and the conservation measures required from partner institutions.

Assessment of a new archive building [sub-heading]

The corrosion aggressiveness of the atmosphere within a multi-story building made of reinforced concrete which was to be used as an archive for paper documents was determined using silver and copper sensors. The building's concrete was poured during winter. The upper floors were completed at below-freezing temperatures, so an antifreeze agent containing urea was added to the concrete. Urea decomposes slowly in concrete releasing ammonia to the surrounding environment. Indeed, the air in the top floors has a typical ammonia odour. It is believed that ammonia in the air is not harmful to the documents but might be dangerous for the metallic parts of stored objects made of copper or brass. A stable temperature of 15 °C and relative humidity of 52 % is maintained in the archive.

An AirCorr I Plus logger equipped with two highly sensitive sensors, silver 50nm and copper 50nm, was installed in the archive. Initially, the logger was placed on a floor built from urea-free concrete with no ammonia odour. Then, it was moved to a floor with a strong ammonia odour. The aim was to test the effect of ammonia-type air pollutants on the air corrosivity. During the exposure in the odour-free area, the measured corrosion depth of 2.1 nm corresponds to the corrosion rate of 27 nm/year for the silver sensor, see Figure 9. The testing period was not long enough to classify the corrosivity according to the ISO 11844-1 standard but extrapolation of the data yields the IC 2 – Low corrosivity class. The corrosion rate identified at the same location for copper was 5 nm/year (Δh of 0.4 nm) corresponding to the IC 1 – Very low classification. After moving the logger onto the floor with the ammonia odour, the corrosion rate of silver dropped to 16 nm/year and remained constant during whole exposure period. In the case of copper, the corrosion rate was 2 nm/year and it slowly decreased.

Surprisingly, the corrosivity on the floor with the ammonia odour was lower than in non-polluted areas. The surface of copper was analysed by XPS after the exposure. The film of corrosion products contained a significant amount (app. 50 %) of copper (II) and nitrogen bound up in an organic compound. Since urea is known for its corrosion inhibition toward copper, adsorption of urea from the atmosphere onto the metallic surface might be the reason for the reduction in the corrosion rates of copper and silver during exposure on the upper floor. The study showed that the locations made with the urea-modified concrete were safe for documents with copper and bronze parts, at least in the short term. The effect of this specific environment on other types of stored materials and its long-term effect on copper and copper-alloy materials is under study.

A quartz crystal microbalance logger was exposed alongside the AirCorr I Plus logger. It recorded a mass gain of the copper- and silver-coated crystals. The corrosion build-up after 38 days was 1.6 nm and 0.9 nm for the silver and copper sensors, respectively [18]. When the AirCorr data on corrosion depth are recalculated to corrosion build-up using Eq. (2), the results are 3.5 and 0.8 nm, respectively. For silver, the following values were used for the calculation: $\rho_M = 10.5 \text{ g cm}^{-3}$, $c = 1.15$ [12] and $\rho_{CP}(\text{Ag}_2\text{S}) = 7.3 \text{ g cm}^{-3}$

³ [13]. Silver sulphide is dominating on metal objects exposed to indoor atmospheres [16] and was assumed to represent density of the entire layer of corrosion products. Although the build-up on silver differs by a factor of 2, identical corrosivity classification was provided and the measurements are in a reasonably good agreement.

Regular air quality monitoring of indoor premises [sub-heading]

The Danish Royal Library considered AirCorr loggers as a possible replacement for passive sampling, which is carried out regularly at different locations within the institution. The high cost and delay of at least 2 months between the samplers' deployment and return of the results are considered drawbacks of the passive sampling method.

An Ag-50nm silver sensor was used. The monitoring was carried out at three locations over a total of 5 months. It started in a small room containing manuscripts with low air exchange, Location 1. Passive sampling showed elevated concentrations of acetic and formic acids. The logger was then moved to storage with air filtration and climate control, Location 2. Acetic acid was not detected and the concentration of formic acid was very low in the second location. Finally, the monitoring was carried out in a visitor centre with low levels of organic acids but non-negligible outdoor pollution in form of SO₂, NO₂ and O₃, Location 3. Cumulative data for the silver sensor along with the results of the accompanying passive samplers and the relative humidity record are shown in Figure 10. The corrosion depth of silver measured in the first 30 days at each of the locations reached 2.0, 0.2 and 4.8 nm, respectively. The air quality classifications according to the ISO 11844-1 standard were IC 2 – Low, IC 1 – Very low and IC 2 – Low [12]. Following the Sacchi and Muller recommendation, S1, Extremely pure class would apply to the first two premises and S2, Pure to the last one [16].

Location 2 with tight air quality control was one order of magnitude less corrosive than Location 1 with elevated levels of organic acids. The highest corrosivity was found in the visitor centre (Location 3), which was open to outdoor air containing typical urban pollutants, including sulphur dioxide, nitrogen dioxide and ozone. Although silver is not particularly sensitive to these compounds, the last two have some effect on its corrosion stability.

Study on the optimal cleaning procedure of brass inlays [sub-heading]

Restorers at the Louvre Museum were searching for the optimal cleaning procedure for the engraved brass inlays in a valuable wooden cabinet attributed to André-Charles Boulle that had been selected for an important exhibition. The engravings, made from alpha-phase brass containing 35 wt.% zinc, had been partially damaged by previous cleanings. About 0.5 mm (500 nm) of the initial inlays' thickness had already been removed and the restorers had to be sure that any technique used for the cleaning would be as gentle as possible. Studies were carried out using the AirCorr system to measure reduction in metal thickness. Because brass sensors are only available at a thickness of 10 µm, which is not extremely sensitive, a bronze CuSn8-

400nm sensor was used for the initial measurements. Four cleaning procedures were applied and changes in the corrosion depth of the sensor were monitored. In addition, roughness measurements and microscopic evaluation were carried out to assess the outcome of each cleaning technique.

The data obtained are plotted in Figure 11. Several of the treatments resulted in good results with limited material loss, including the application of an animal glue with triammonium citrate (TAC), which is also used to restore the marquetry and which resulted in a nice surface appearance; ivory black, a very gentle abrasive; and micromesh 1200, a corundum-based abrasive. The corrosion depths caused by these cleaning procedures was in the range of 9 to 17 nm. On the other hand, the procedure using triethanol amine (TEA) and Pemulen gel led to material removal corresponding to 181 nm and thus cannot be considered a gentle technique. Roubo lacquer is a Sandarac-based resin dissolved in alcohol, which is named after a French cabinetmaker who wrote "The Art of the Carpenter" in 1769. It was applied and then removed without causing any metal corrosion.

Since the composition of the applied sensor was different from the brass of the inlays, the tests will be repeated with CuZn37-10µm sensors. Although the composition and microstructure is not (and cannot) be identical to that of the historical material and the material loss due to cleaning would probably be somewhat different, it is believed that the obtained data allow for a comparison of the various cleaning procedures.

Systematic classification of air quality using copper sensors [sub-heading]

Corrosion monitoring by two types of ER loggers, including AirCorr, was used to assess the air quality in numerous predominantly indoor cultural heritage locations with the aim of responding to questions frequently asked by conservators and curators on the appropriateness of the conservation conditions in a given museum, showcase or storage. Changes in corrosion depth of Cu-500nm copper sensors were followed in the course of a year either by intermittent measurements or by continuous monitoring. Results of studies performed in twenty museums, libraries and archives situated in France are presented elsewhere [14]. Most of the locations were heated (twenty-six showcases, eleven exhibition rooms, fifteen storages, six crates), but in sixteen sites the climate was not controlled, including two outdoor exposures.

The data obtained on the corrosion depths of the copper sensors were interpreted using the ISO 11844-1 standard [12]. 60 % of the environments had very low corrosivities (IC 1) and 5 % were highly corrosive (IC 5). The corrosivity was found to be low for two-thirds of the heated rooms and high for 3%. In half of the permanent exhibitions, the corrosivity was found to be very low (IC 1); it was low (IC 2) or medium (IC 3) for the rest.

The ER technique showed to be a very efficient tool for assessing the conditions of conservation in archives, libraries and museums. It allowed for comparison of the conditions of conservation in particular locations and for assessment of any applied countermeasures. A drawback of the currently available standard is the necessity that the probe be exposed for a full year in a given environment. Due to the high sensitivity of the ER measurement, reproducible results can be obtained in a shorter period. The ISO 11844-1 classification

was thus compared to the Sacchi & Muller guideline based on 30-day exposures [16]. In most cases, good correlation to ISO 11844-1 was obtained.

Classification of air quality with lead sensors [sub-heading]

The air quality in low-corrosive environments can be qualified by the reactivity of copper [15], copper and silver [16] or copper, silver, carbon steel and zinc [12]. Parallel exposures of more than one metal are carried out due to the different sensitivities of different metals to the presence of specific pollutants. For example, carbon steel is particularly sensitive to chloride, silver to hydrogen sulphide and copper to sulphur dioxide [19]. However, none of these metals is very sensitive to the carboxylic acids that are repeatedly reported as important pollutants in enclosed locations in indoor cultural heritage institutions such as showcases and cabinets. Concentrations of formic and acetic acids released from hemicellulose-containing wrapping papers and cardboards; exhibited or stored objects made of wood, paper and some plastics; and conservation and showcase materials can vary from negligible to hundreds or even thousands of ppb [20–27]. The acids are harmful to metals, calcareous materials and possibly also paper and some plastics. Lead is particularly sensitive to the presence of vapours of carboxylic acids.

Because of accelerated corrosion in air polluted with formic and acetic acid and the number of lead objects in museums, it is of interest to use lead as an additional sensing material. Unfortunately, no current standard includes lead. Little is also known about the kinetics of lead corrosion in such environments due to the low sensitivity of currently available techniques. The Pb-400nm and Pb-25 μ m sensors developed for the AirCorr loggers provide a unique opportunity to acquire valuable knowledge on lead corrosion and establish an air corrosivity classification system for this metal. The lead sensors were exposed at 15 locations within the end-user testing programme for 30 days or longer. Some of the locations were reportedly corrosive towards lead objects and others were supposed to be benign. The corrosion depths registered within first 30 days of exposure varied from 0.1 to 107 nm. Examples of two consecutive measurements in the Australian War Memorial in a showcase where the lead pieces of a ship model corroded are given in Figure 12. Corrosion rates of 90 and 104 nm/30 days were recorded. Although the work is still in the beginning stages and much more corrosion and supporting data need to be obtained to establish a classification system for lead, a preliminary proposal dividing atmospheres into four classes based on the corrosion depth of lead after 30 days of exposure is outlined in Table 2. It is possible that one more class will be needed to cover extremely polluted and corrosive environments.

It is interesting to note that any classification based on exposure of copper and silver is irrelevant for lead objects. Several of the experiments conducted with lead were accompanied by parallel exposure of silver and/or copper sensors. Even in conditions where the corrosion rate of lead reached over 10 nm/30 days, i.e. Class L 3 according to the proposal in Table 2, IC 1 – Very low or IC 2 – Low classes were obtained for silver and copper.

High-corrosive environment in a paper mill [sub-heading]

Besides the cultural heritage sphere, the monitoring system was tested in selected highly demanding environments in order to prove its robustness. As an example, the results from an application in a sludge press building of a pulp and paper manufacturing facility located in Southern USA are shown in Figure 13. The principal corrosive factors are a high concentration of 100–130 ppb of H₂S, high humidity and deposition of chemically-active aerosol. During the first seven days of exposure, 340 nm of a Cu-500nm and 143 nm of a Ag-500nm sensor corroded, corresponding (after linear extrapolation) to corrosion rates of 19 and 8 µm/year and corrosion build-ups of 3400 and 1100 nm/30 days, respectively. Such corrosivity is outside the scale of the ISO 11844-1 standard and in the most corrosive class according to other standards and recommendations.

The curve in Figure 13 shows the high reactivity of the sensor. The actual corrosion rate corresponded to changes in RH. When the RH crossed 80 %, the corrosion rate increased significantly. The corrosion rate was the lowest in a period where the RH was about 50–60 % (0.3 nm/hour). It increased above 1.5 nm/hour when the RH was over 80 % and it reached a maximum of 3.7 nm/hour when the RH exceeded 90 %.

Conclusions [heading]

The developed technology proved to provide extreme sensitivity at a sub-Ångström ($<10^{-10}$ m), i.e. atomic, level allowing for real-time corrosion monitoring even in low-corrosive indoor cultural heritage premises. Due to short response times, immediate countermeasures can be applied in case of an increase in the atmospheric corrosivity.

It was shown that the technique is reproducible with the standard deviation for parallel measurements at ± 20 % or lower for metals corroding mostly uniformly in a given environment. Since the response corresponds to the maximal cross-section reduction and is thus close to the maximal depth of corrosion attack, the resulting corrosion depth is usually somewhat higher than that found by methods measuring the average corrosion depth.

A widespread testing programme was conducted in partner museums, archives, libraries and other institutions to demonstrate the potential of the real-time reactivity monitoring by the ER technique. AirCorr loggers were successfully applied for the characterisation of air quality control in indoor locations, during transport and in temporary exhibitions; assessment of new buildings and storage facilities; and fundamental studies of optimal conservation and storage procedures. Unique sensors made of lead and some alloy materials can provide useful insight into corrosion of these materials that was difficult or even impossible to acquire earlier. A first outline of a classification system for lead, which is particularly sensitive to presence of carboxylic acids, is proposed.

It is believed that the technique has a large potential as an independent method for monitoring air quality in facilities displaying and storing valuable objects of cultural heritage.

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Figures

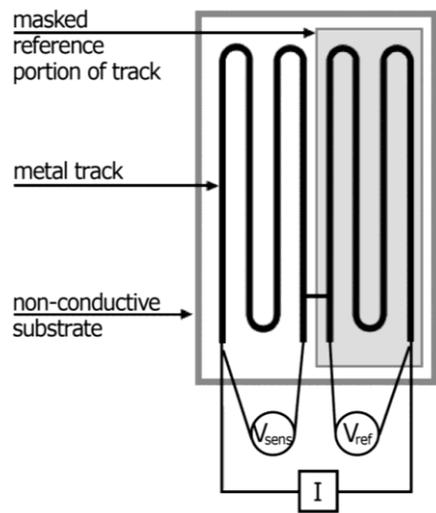


Figure 1 Schematic drawing of corrosion sensor

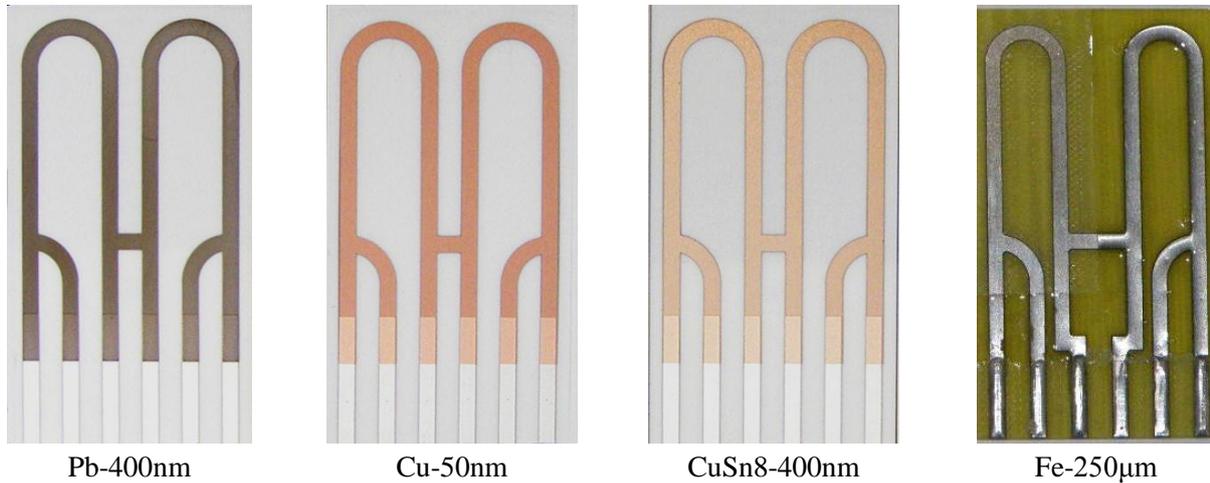


Figure 2 Photographs of selected corrosion sensors



Figure 3 Three versions of corrosion loggers

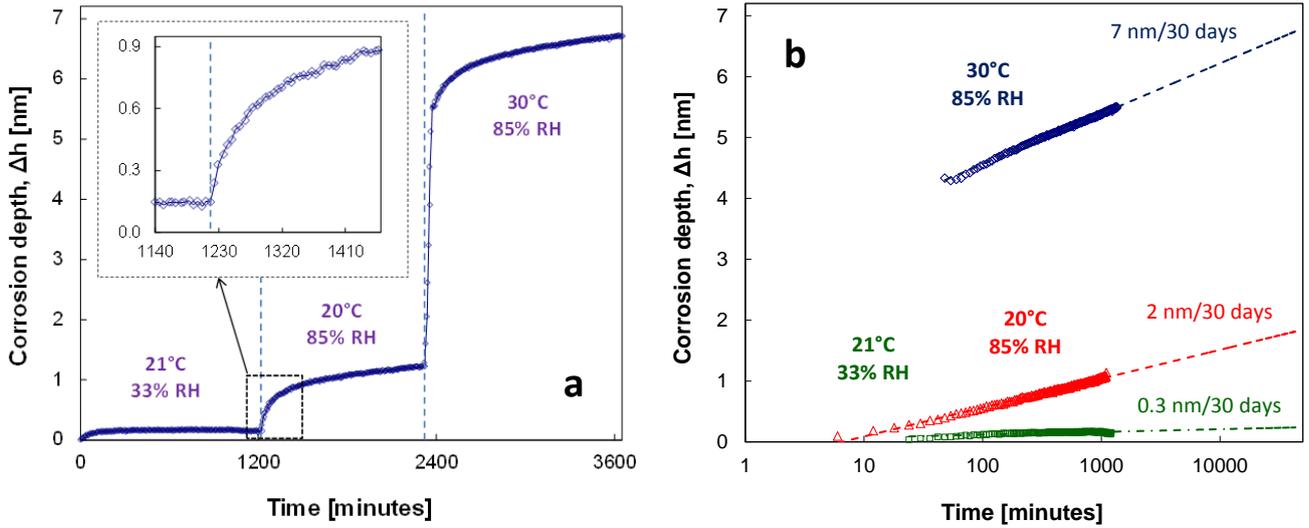


Figure 4 Corrosion depth measurement in air using a Cu-500nm sensor (a) and extrapolated stabilised parts of the corrosion depth curve (b)

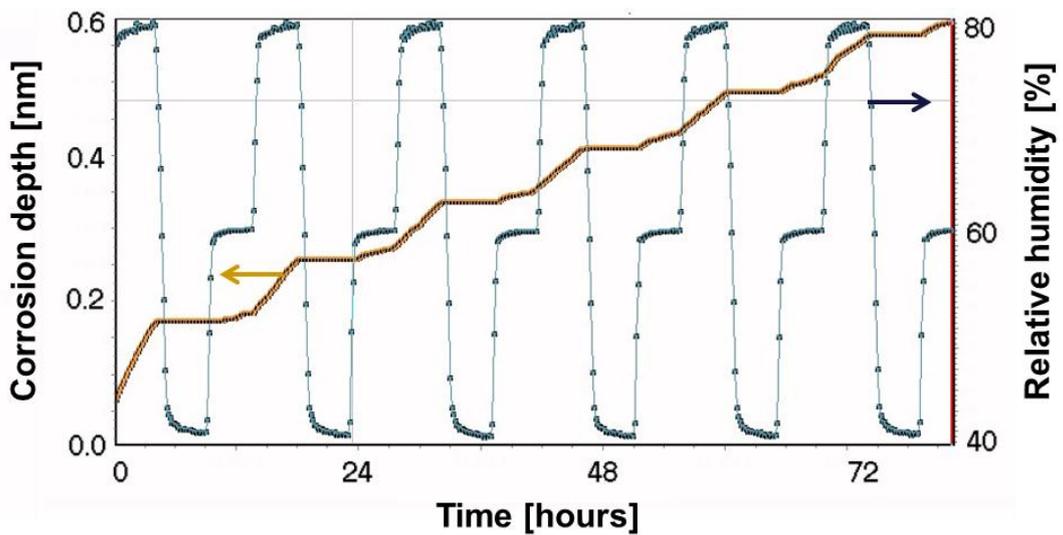


Figure 5 Record of corrosion depth of Ag-50nm sensor during humidity cycling in air at 25 °C

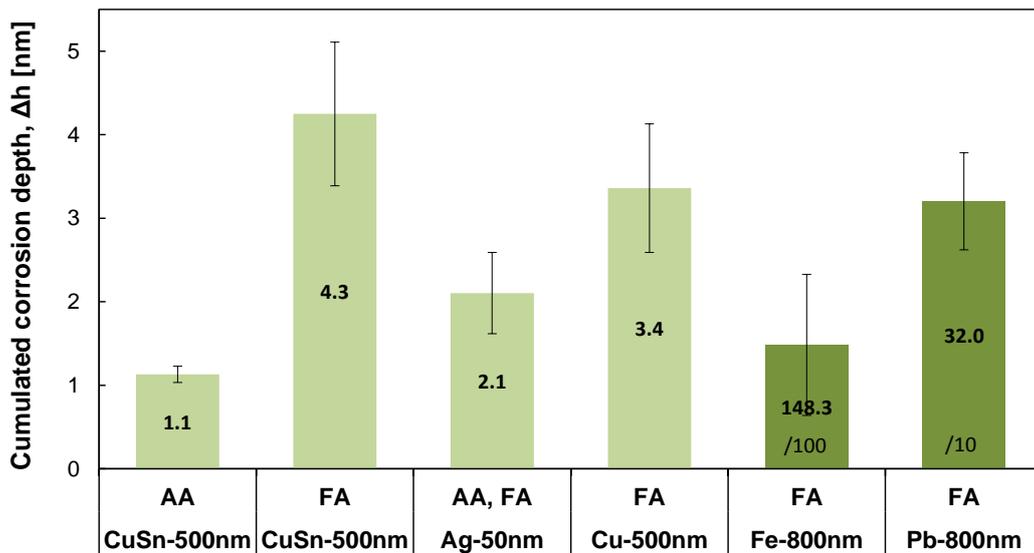


Figure 6 Corrosion depth measurements for different sensors in air at 20 °C containing acetic acid (AA) and formic acid (FA) with error bars showing the standard deviation; exposure conditions differed for each sensor type

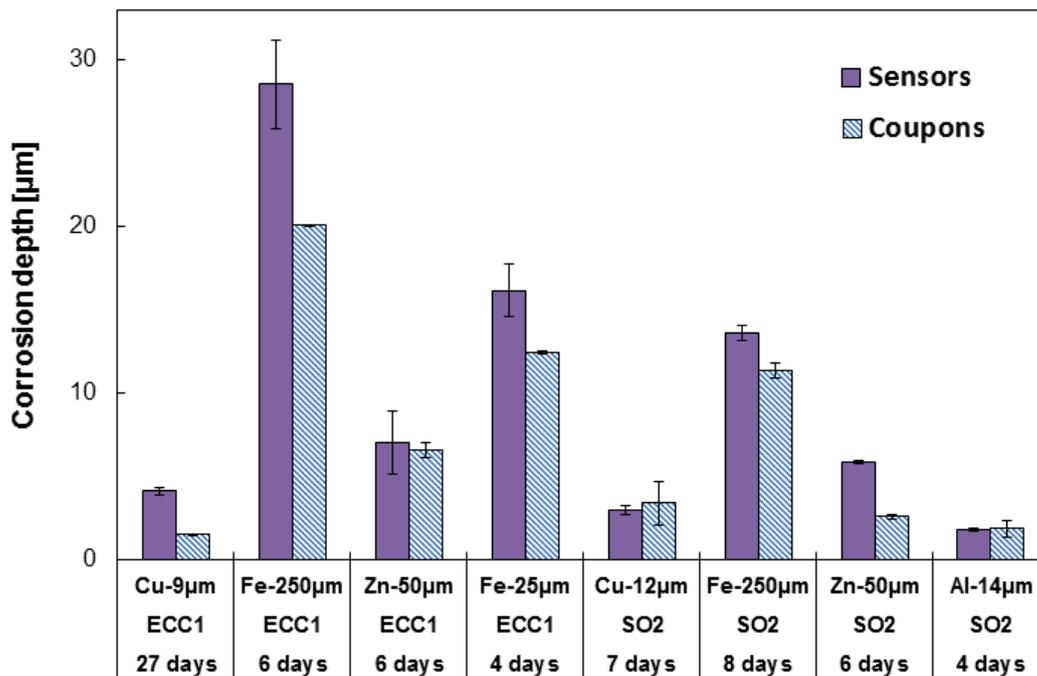


Figure 7 Comparison of corrosion depth measured using AirCorr sensors and metal coupons in a cyclic accelerated test comprising sample spraying with NaCl (ECC1) and in air containing SO₂ (SO2); exposure duration differed for each sensor type

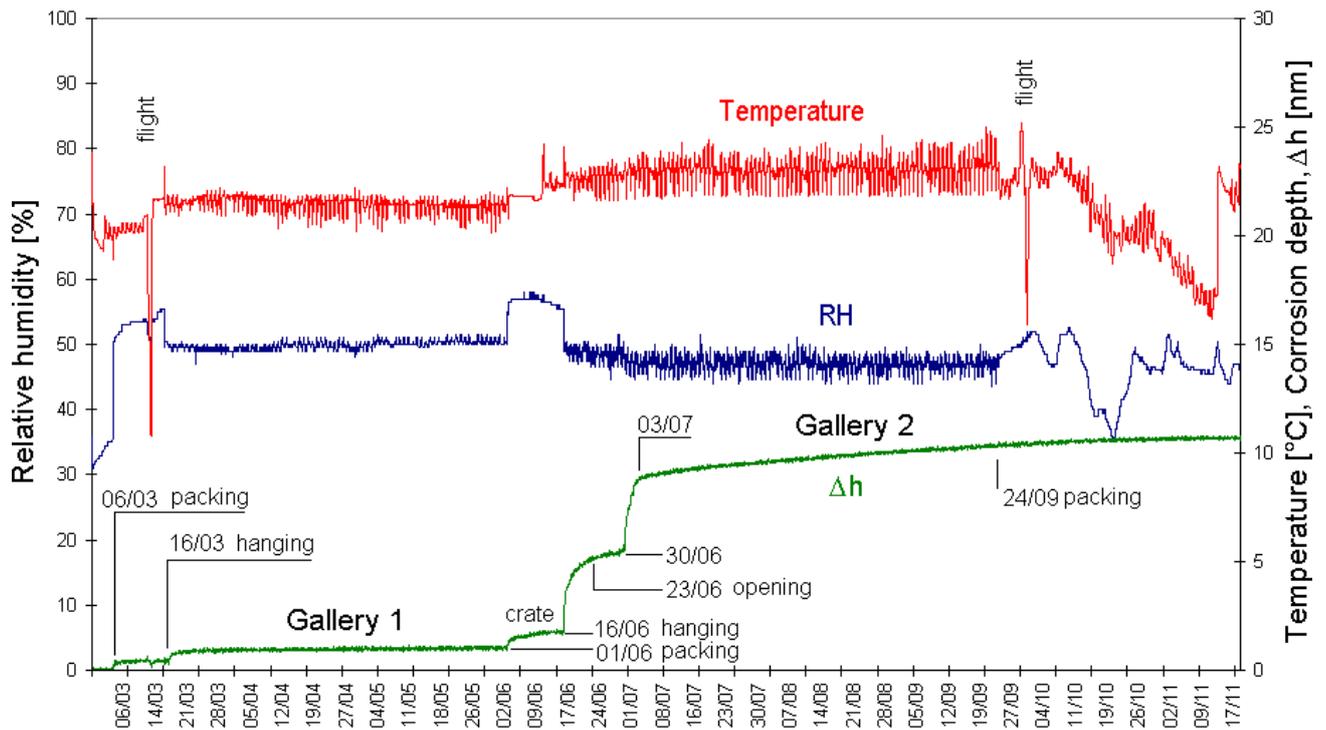


Figure 8 Corrosion depth, temperature and relative humidity during transport and exhibition of a tapestry loaned by Louvre museum

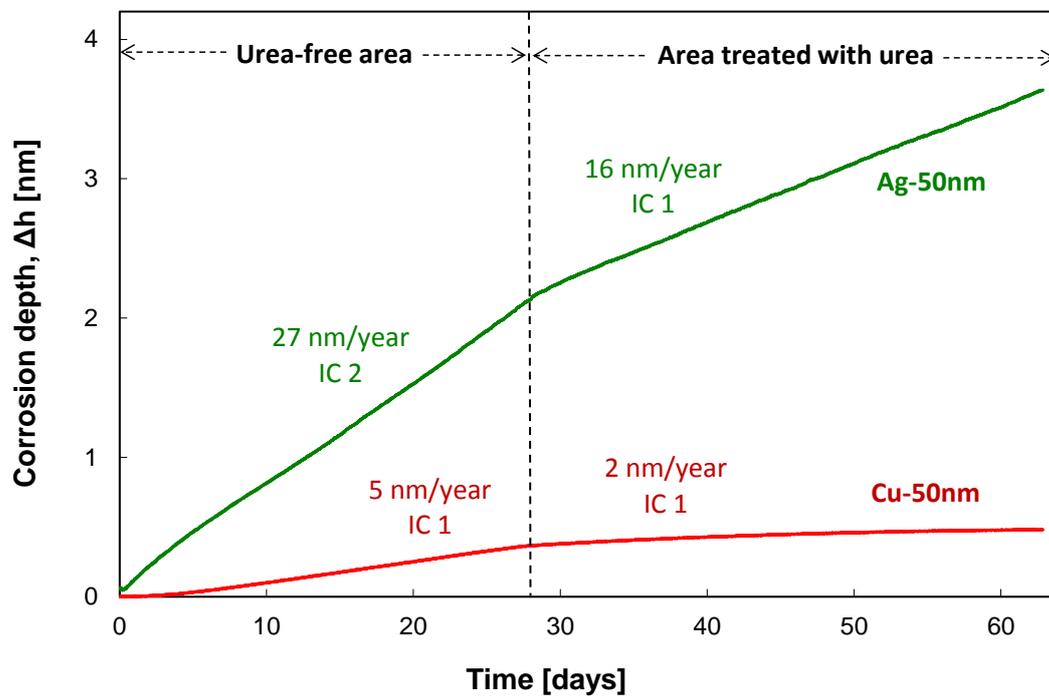


Figure 9 Record of silver and copper corrosion depth in an archive building

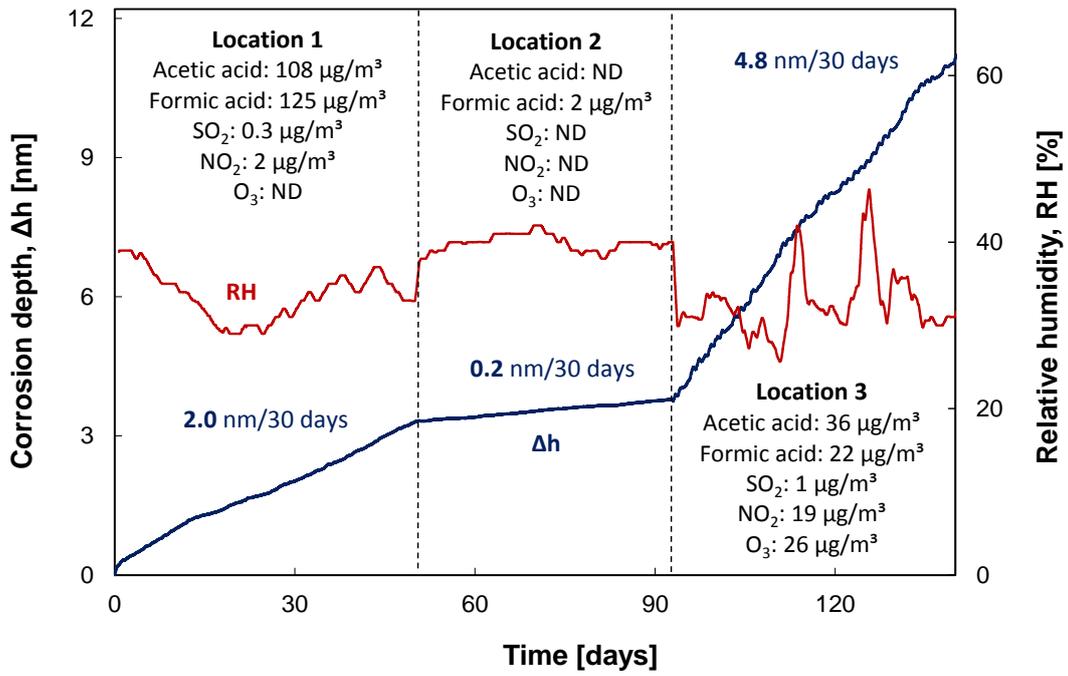


Figure 10 Corrosion depth recorded on Ag-50nm sensor at three locations in The Danish Royal Library; ND: Not detected

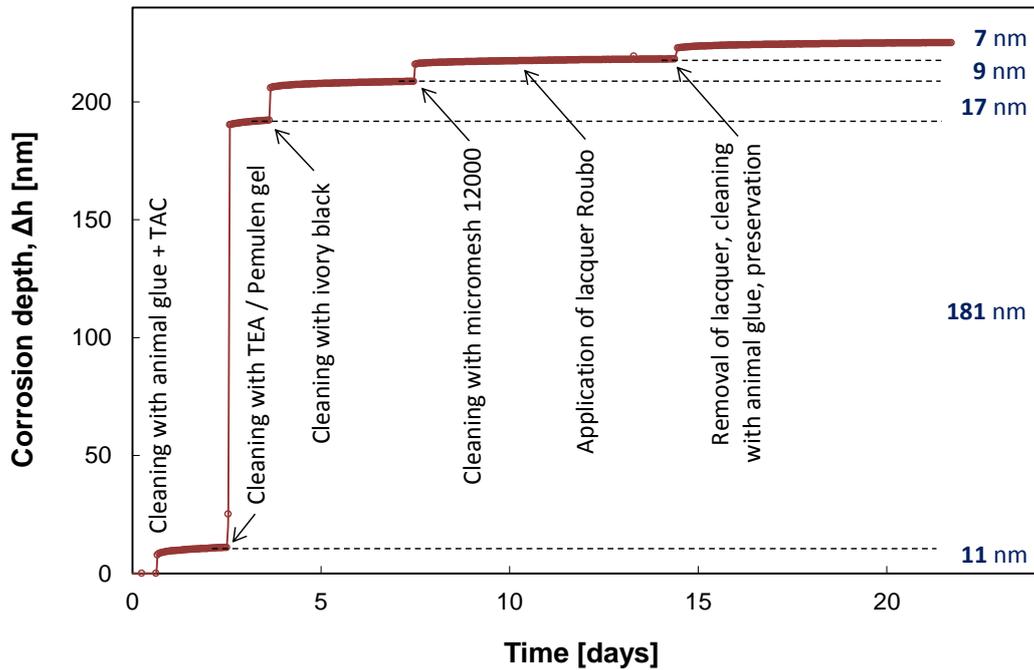


Figure 11 Cleaning of a CuSn8-400nm sensor using different techniques

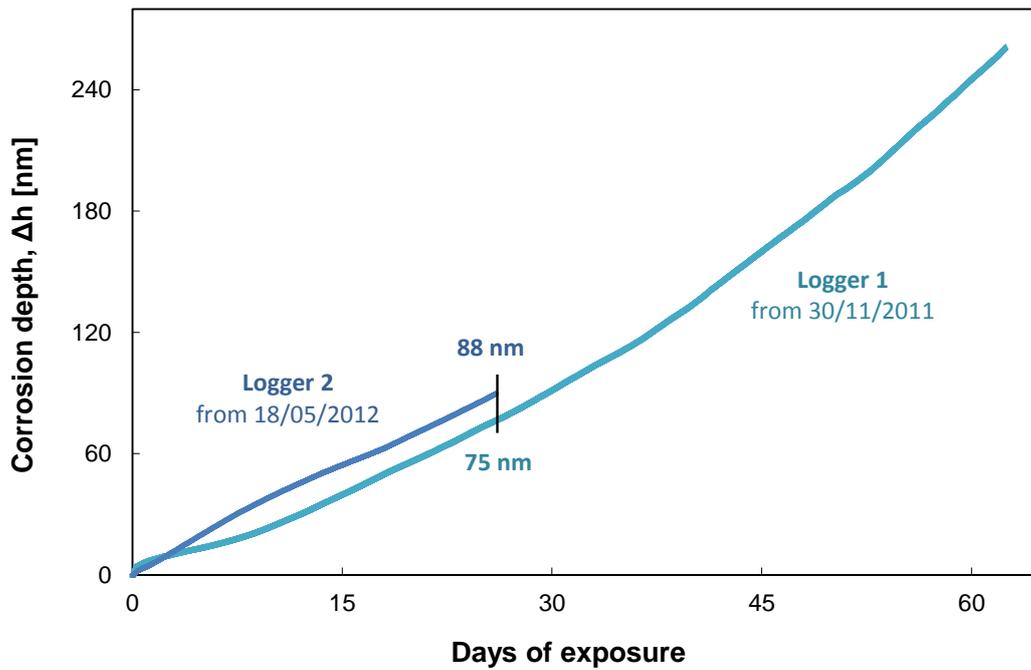


Figure 12 Corrosion depths measured using two Pb-400nm sensors in a showcase of The Australian War Memorial in which lead pieces on a ship model have been found to corrode

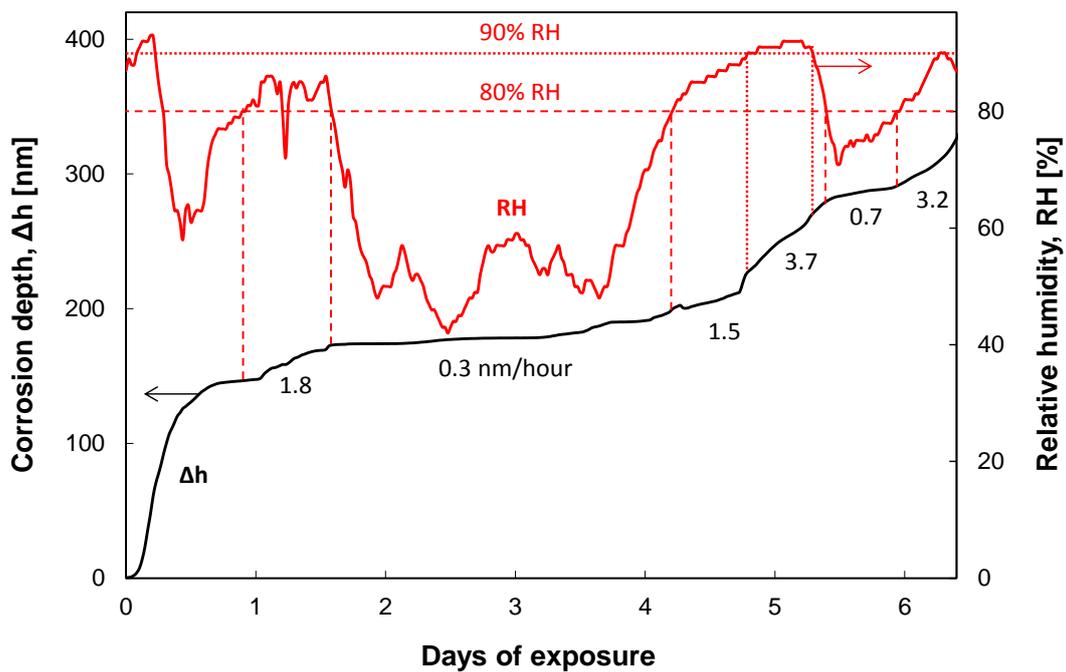


Figure 13 Corrosion depth on a Cu-500nm sensor and relative humidity in a sludge room in a paper mill; horizontal lines indicate 80 and 90% RH levels; numbers by the corrosion depth curve give the corrosion rate in the given segment in nm/hour

Tables

Table 1: Types and thicknesses of corrosion sensors

Material	Indoor, high sensitivity	Indoor, long lifetime	Outdoor, high sensitivity	Outdoor, long lifetime
Copper	50 nm	500 nm	5 µm	12 µm
Silver	50 nm	500 nm		–
Lead	400 nm	25 µm		
Iron/steel	800 nm	25 µm		250 µm
Zinc	–	25 µm		50 µm
Aluminium	–	14 µm		
Tin	–	10 µm		
Bronze	400 nm		5 µm	
Brass	–	10 µm		

Table 2: Preliminary proposal for air corrosivity classification for lead

Class	Corrosion rate [nm/30 days]	Visual lead corrosion	Carboxylic acids
L 1 – Pure	<3	Not observable	Negligible to low (ppb to tens of ppb)
L 2 – Clean	<10	Low	
L 3 – Contaminated	<50	Visible	Elevated (100 ppb or higher)
L 4 – Polluted	≥50	High	