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SCIENTIFIC PAPER

STANDARDIZED ASSESSMENT OF CULTURAL HERITAGE ENVIRONMENTS BY ELECTRICAL RESISTANCE MEASUREMENTS

Michel Dubus[1], Tomas Prosek[2]

1. Centre de recherche et de restauration des musées de France, 14 quai François Mitterrand, 75001 Paris, France
2. Institut de la Corrosion / French Corrosion Institute, 220 rue Pierre Rivoalon, 29200 Brest, France

corresponding author:
michel.dubus@culture.gouv.fr

Corrosion monitoring by resistivity measurement was used to assess the environmental conditions in cultural heritage institutions, with the aim to provide advice on the preservation conditions in museums, showcases or storage areas. Changes in corrosion depth of thin copper sensors were followed during a year. The results of studies in 13 museums, libraries and archives are presented. Of these, 38 locations were heated (23 showcases, 8 exhibition rooms, 14 storage areas), at 7 locations the climate was not controlled.

The electrical resistance (ER) technique showed to be a very efficient tool to assess the environmental conditions in archives, libraries and museums. It allowed for comparison of the conditions in particular locations and for assessment of the applied control measures. Due to high sensitivity of ER measurements, reproducible results can be obtained in a month, in comparison to a year required by current standards.

The obtained data on corrosion depth of copper sensors are interpreted using ISO 11844-1 standard, which classifies environments into five corrosivity classes. 60% of the environments were of "Very low corrosivity (IC1)", or almost 70% of the heated rooms, and two thirds of the permanent locations. "High corrosivity (IC4)" was found in 5% of the monitored locations.

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1 Introduction

Indoor atmospheric corrosion was first studied in the 1930s to monitor switchboards, then in the 1960s for computer centres, but only from the 1970s on, to also monitor cultural heritage.[1] In France, indoor air quality has been studied for ten years,[2] but it remains poorly documented in cultural heritage environments.

In museums, libraries and archives, pollutants can originate from outdoors, from building materials or from the collections themselves.[3] Pollutant gases can affect collections more or less fast depending on their concentration: sulfur dioxide (SO_2) is corrosive to metals, alloys, minerals, attacks cellulose, dyes, pigments and photographs, leather; nitrogen dioxide (NO_2) promotes the action of SO_2 (the role of moisture is less important in indoor air in industrial and urban environments); hydrogen sulfide (H_2S) blackens silver, tarnishes copper and its alloys, some pigments and dyes; organic acids corrode steel, copper alloys, lead, zinc, nickel, calcium carbonate.[4]

The main objectives of the study were to assess the quality of indoor environments where objects of cultural heritage are displayed or stored, and to provide conservators responsible for the collections with information on the relative quality of an environment. If elevated air corrosivity was found, a countermeasure would be proposed and applied.

The ability to predict indoor corrosion rates based on information on only a few pollutant concentrations is very limited and cannot be performed with high accuracy yet. Nevertheless, there are techniques that allow following the change in corrosion rate caused by changes in the indoor environment.[1] In this study, corrosivity of indoor air was evaluated by measuring corrosion depth of copper sensors exposed in given environments for a year, using the electrical resistance measurement technique. Although it is principally relevant for objects made of the corresponding metal, it is often used for general air corrosivity assessment, for objects made of a wide variety of materials. The growth of corrosion films on copper coupons gives an excellent indication of the type and concentration of pollutants, and its measurement was used here to assess and classify the conditions of conservation in ethnographic, science and technology museums, archives and libraries. The results, interpreted with the help of the ISO 11844-1 standard[5] and the Sacchi-Muller guideline,[6] give an overview of the environmental conditions in some French cultural heritage institutions.

2 Experimental

2.1 ER Technique

Several methods such as mass gain or mass loss of metal coupons,[7-11] quartz crystal microbalance,[12-14] coulometric reduction,[15] electrical[16] and optical[17-18] methods can be used in corrosion monitoring in cultural heritage environments with low corrosivity. Due to its high sensitivity and robustness, the ER technique was selected for this study. Its principle is simple: the change of electrical resistance of a thin metal layer applied on an insulating substrate is measured, and as the metal corrodes, the cross-sectional area of the layer decreases and the ER increases. A part of the metal track is protected and thus serves as the reference to compensate for resistivity differences due to varying temperature. The corrosion depth (CD) of the metallic sensor is then calculated from the initial and actual ER. The technique is described in detail elsewhere.[16,19-20]

Two devices were used. From 2002 to 2007, sensors TF50 of model 610 (Rohrback Cosasco, Santa Fe, CA) with the thickness of 25 nm were applied.[21] They are well suited to indoor environments with low-corrosivity. The resolution, reproducibility of measurement and precision were 0.1%, ±0.5% and ±10%, respectively. Single measurements were made with a CK-4 Corrosometer® with a sampling period of about a month. From 2006 to 2011, data loggers and sensors developed in European research projects were used.[22-23] Copper sensors of 500 nm with a resolution of 0.1 nm were attached to electronic loggers allowing for permanent measurement and data storage.[24]

Copper sensors were chosen for their sensitivity to humidity and a broad range of pollutants such as H_2S, SO_2 and organic acids.[5] The measurements were not duplicated in order to reduce costs. In parallel, temperature and relative humidity were registered. In selected locations, concentrations of pollutants were measured using passive samplers.

2.2 Corrosivity Classification

The ISO 11844-1 (Corrosion of metals and alloys - Classification of low corrosivity of indoor atmospheres - Part 1: Determination and estimation of indoor corrosivity) standard was used to interpret the results. The time of exposure was greater or equal to one year as required by this standard. It is specially written for low corrosive environments such as museums and monuments and includes an annex on ER measurements. It describes procedures to characterize indoor atmospheric environments of low corrosivity that can affect metals and metallic coatings during storage, transport, installation or operational use, and to estimate indoor corrosivity categories, see Table 1.

In this standard, each corrosivity class is divided into two subsets describing the typical environments of heated or unheated spaces:
- IC1 Very low corrosivity: Heated spaces with controlled stable relative humidity (<40%) without risk of condensation, low levels of pollutants, no specific pollutants, e.g. computer rooms, museums with controlled environment. Unheated spaces with dehumidification, low levels of indoor pollution, no specific pollutants e.g. military equipment storage areas.
- IC2 Low corrosivity: Heated spaces with low relative humidity (<50%) with certain fluctuation of relative humidity without risk of condensation, low levels of pollution, without specific pollutants e.g. museums, control rooms. Unheated spaces with only temperature and humidity changes, with no risk of condensation, low levels of pollution without specific pollutants, e.g. storage rooms with low frequency of temperature changes.
-IC3 Medium corrosivity: Heated spaces with risk of fluctuation of temperature and humidity, medium levels of pollution, certain risk for specific pollutants, e.g. switch board in power industry. Unheated spaces with elevated relative humidity (50-70%) with periodic fluctuation of relative humidity, without risk of condensation, elevated levels of pollution, low risk of specific pollutants, e.g. churches in non-polluted areas, outdoor telecommunication boxes in rural areas.
- IC4 High corrosivity: Heated spaces with fluctuations of humidity and temperature, elevated levels of pollution including specific pollutants, e.g. electrical service rooms in industrial plants. Unheated spaces with high relative humidity (up to 70%) with some risk of condensation, medium levels of pollution, possible effect of specific pollutants, e.g. churches in polluted

Corrosivity class	IC1 Very low	IC2 Low	IC3 Medium	IC4 High
Corrosion depth (nm/year)	≤5.6	≤22	≤101	≤224

Table 1: Corrosivity classification of indoor atmospheres for copper according to ISO 11844-1.

Corrosivity class	C1 Extremely pure	C2 Pure	C3 Clean	C4 Slightly contaminated
Corrosion build-up (nm/30 days)	< 9	< 15	< 25	< 35

Table 2: Corrosivity classification of indoor atmospheres according to Sacchi-Muller; 6 in terms of corrosion build-up on copper (thickness of formed corrosion products).

areas, outdoor boxes for telecommunication in polluted areas.

- IC5 Very high corrosivity: Heated spaces with limited influence of relative humidity, higher levels of pollution including specific pollutants like H_2S, e.g. electrical service rooms, cross connection rooms in industries without efficient pollution control. Unheated spaces with high relative humidity and risk of condensation, medium and higher levels of pollution, e.g. storage rooms in basements in polluted areas.

However, it is not always possible to expose a sensor or coupon for a year, especially during transport and in temporary exhibitions. In addition, a year may be too long a period in case the air corrosivity is elevated and valuable objects are at risk of rapid degradation. The only currently available short-term alternative for cultural heritage is the Sacchi-Muller guideline. [6] It classifies air corrosivity based on the thickness of the layer of corrosion products formed within 30 days of exposure, see Table 2.

Calculations are based on the electric charge needed for electrochemical reduction of the corrosion products. Two systematic errors are introduced: (i) the apparent instead of the real surface area is used; (ii) the density of the corrosion products is not known but only estimated.

To recalculate the thickness of the corroded metal, i.e. the corrosion depth, to the thickness of the layer of corrosion products, three pieces of information are needed: (i) the density of the metal, (ii) the density of the corrosion products, (iii) the ratio between the mass of the formed corrosion products and the mass of corroded metal. The latter two parameters are not known and must be estimated. The density of the corrosion products, ρ_{CP}, is assumed to be about 6.0 g•cm^{-3} for cuprous oxide, Cu_2O,[25] which is usually dominating on copper objects exposed to indoor atmospheres.[6] It was assumed to represent the density of entire layers of corrosion products. The ratio between the mass of the formed corrosion products and the mass of corroded metal, *c*, was obtained from ISO 11844-1.[5] It is 1.5 for copper. Thus, the following equation can be used to estimate the corrosion build-up, *b*, from corrosion depth, Δh:

$$b = \rho_M \times c \times \Delta h / \rho_{CP}$$

where ρ_M is metal density, i.e. 8.9 g•cm^{-3} for copper.

2.3 Monitoring Locations

23 showcases, 8 rooms, 14 storage areas have been studied, representing 43 permanent and 2 temporary locations, 38 of which were in heated environments (22 showcases, 8 rooms, 8 storage areas), while 6 storage areas and 1 showcase were in unheated environments. Further details on the locations can be found elsewhere.[26]

3 Results

The data in terms of corrosion depth measured within a year are plotted in Fig. 1.

80% of the premises are classified as IC1 and IC2, and are therefore well suited to keep cultural heritage collections according to the standard. The corrosivity was very low (IC1) in 60% of the heated spaces, and

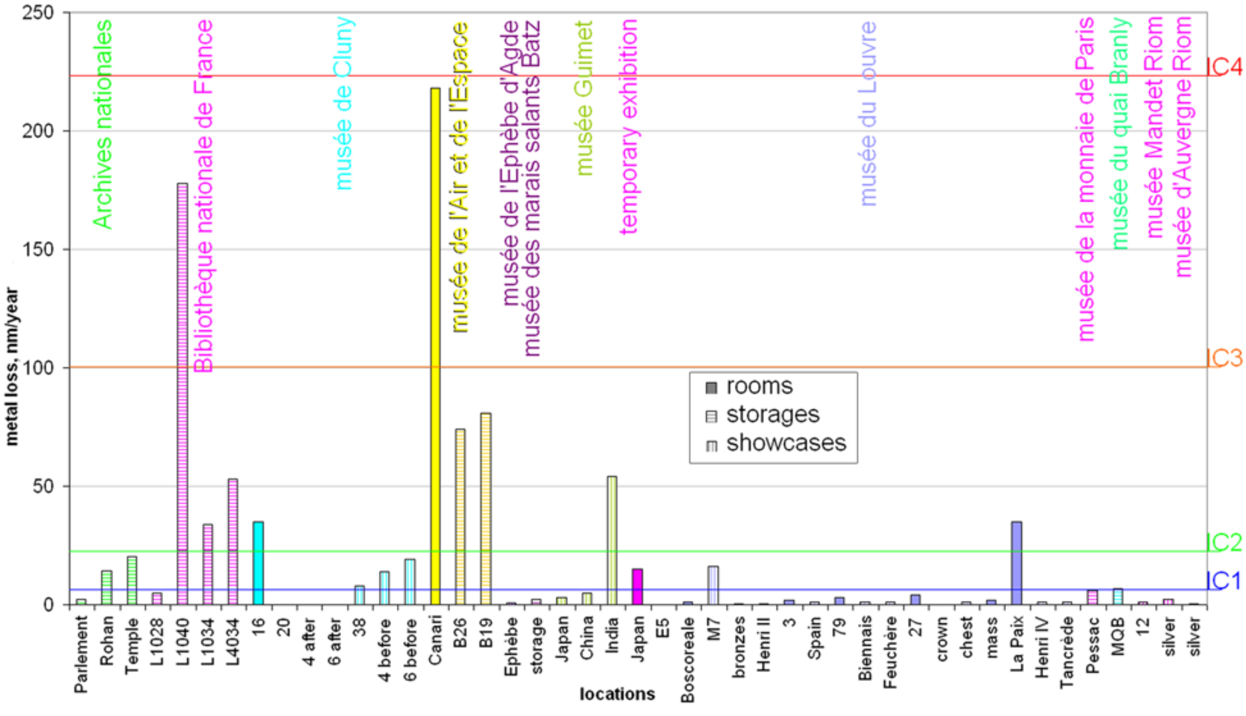

Figure 1: Corrosion depth in nm/year and classification according to ISO 11844-1.

Figure 2: Oiseau Canari at the Musée de l'Air et de l'Espace.

unheated spaces such as the *Galerie du parlement* of the National Archives or the showcases of the *Musée d'Auvergne* in Riom. In 20% of the spaces, corrosivity was low (IC2): in the *Cluny* museum, the results show that corrosivity in the showcases 4 and 6 diminished after improvements were carried out; oak parts were covered with a vapour barrier and the plywood replaced with Dibond, a composite material consisting of a core of low density polyethylene (LDPE) between two sheets of aluminium;[27] low corrosivity was also found in the unheated storage of the *Musée de la Monnaie* in Pessac.

The corrosivity was medium (IC3) or high (IC4) in 20% of the monitored locations. The elevated corrosivity was due to different reasons. In the confined storages of the *Bibliothèque nationale de France*, it was due to the emission of acetic acid and formaldehyde by the collections themselves and by the packaging materials, resulting in concentrations of pollutants above the limit tolerated by the ISO 11799 standard.[28] Similarly, the concentrations of acetaldehyde exceed 100 µg m^{-3} in room 16 of the *Cluny* museum, where the floor and the showcases are made of oak. At the *Louvre*, room 31 is directly connected to outdoors via the museum entrance under the pyramid. However, it was not possible to explain why the corrosion was elevated in the *India* showcase compared to other showcases of the *Guimet* museum; the materials of this showcase are inert (stone, glass and metal) and the climate is supposed to be suitable; the average temperature during the corrosivity measurement was 22±1 °C, the average relative humidity 51% (ranging from 32 to 58%). At the *Musée de l'Air et de l'Espace,* the corrosion rate was high (IC4) in the Bernard 191 GR n°2 *Oiseau Canari* aircraft made of plywood (Fig. 2), and medium (IC3) in the B19 and B26 unheated hangars.

4 Discussion

The classification according to the ISO 11844-1 standard enables the interpretation of results according to heating practice, intended length of exposure and type of premises such as exhibition rooms, showcases, and storage areas. 84% of permanent locations and all the temporary ones were heated. The corrosivity was very low (IC1) in 66% of the cases, low (IC2) in 16% and medium (IC3) or high (IC4) in 18%; it was very low in 33%, low in 42%, and medium or high in 29% of the unheated rooms, see Fig. 3.

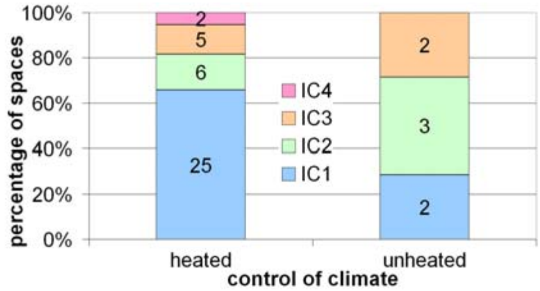

Figure 3: Corrosivity classification of the monitored locations according to ISO 11844-1: heated and unheated.

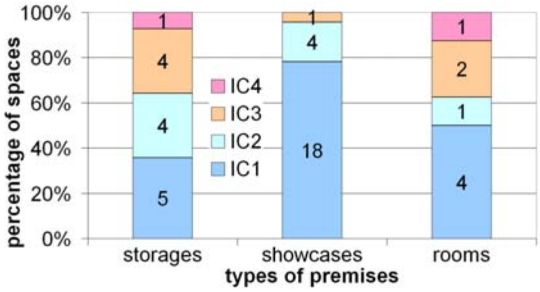

Figure 4: Corrosivity classification of premises by ISO 11844-1 according to their type.

	IC1	IC2	IC3	IC4	Total
C1	44	8	0	0	52
C2	0	4	1	0	5
C3	0	2	4	0	6
C4	0	0	2	0	2
C5	0	0	5	3	8
Total	44	14	12	3	73

Table 3: Cross-correlation of the classifications according to ISO 11844-4 (IC1–IC5) and Sacchi-Muller (C1–C5), based on our 74 measurements.

The corrosivity was very low (IC1) in 5 storage areas, 18 showcases and 4 exhibition rooms; it was low (IC2) in 4 storage areas, 4 showcases and 1 exhibition room, medium or high (IC3) or high (IC4) in 5 storage areas, 1 showcase and 3 exhibition rooms, see Fig. 4.

The ISO 11844-1 and Sacchi-Muller classifications, based on 73 measurements carried out in 14 to 480 days, are compared in Table 3. The corrosion build up values required for the Sacchi-Muller classification were estimated from corrosion depth in the first month of exposure using the equation above. Whatever the time of exposure, the IC1 class of the standard matches the C1 class of the guidelines written by Sacchi and Muller. The classification IC2 is in good correlation with C2 in four cases and undervalued in 8, overvalued in 2 cases. IC3 and IC4 classes are either undervalued in one case and overestimated (10 cases) by Sacchi-Muller. Thus, the classifications are in good agreement in environments of low-corrosivity. The Sacchi-Muller recommendations tends to be somewhat stricter in conditions characterized by elevated air corrosivity.

5 Conclusions

The results presented here provide a benchmark for assessing cultural heritage environments, to compare indoor environments, showcases, storage areas, in either the short term or in the long term. Environments can be classified according to their corrosivity using the ISO 11844-1 standard, taking into account seasonal environmental variations and pollution events. The guidelines by Sacchi and Muller can be used for environments of low corrosivity, with a shorter exposure time of one month.

The ER technique, in combination with continuous environmental monitoring, is seen as an optimal monitoring tool for indoor environments of low corrosivity, where cultural heritage objects are stored or displayed. It allows for rapid feedback on the air quality and development of mitigation measures.

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