Impact of the environmental conditions on the conservation of metal artifacts: an evaluation using electrochemical techniques

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Abstract

Metallic coupons were used to evaluate the environmental conditions in several French cultural institutions. They have been exposed inside and outside display cases and evaluated by electrochemical reduction of the surface products formed during the exposure period. The analytical technique allowed the quantitative detection of different compounds. Since deposition of particulate matter accelerates the rate and selectivity of tarnishing, the use of showcases to exhibit artifacts seems to have a beneficial effect, provided that they don't contain any harmful pollutant.

Introduction

Sources of potentially dangerous environmental conditions are currently being investigated with the aim of minimizing deterioration of cultural artifacts. Because pollutants occur usually in very low concentration inside cultural institutions, their determination is a difficult task, requiring sensitive, relatively expensive and not always accessible techniques. Moreover, even though they are able to detect down to ppb of a given pollutant, this isolated result can hardly define the environment's harmfulness, due to the lack of standard threshold values and to the synergistic effect when several pollutants combine to interact with the material's surface.

Among the methods used to study the impact of the environment on the deterioration of metallic objects, electrochemical evaluation of metallic surfaces previously exposed to a given environment appears to be a very suitable tool. By reducing the products formed on such surfaces, it is possible to resolve the total layer into its major individual chemical constituents. Moreover, the high sensitivity of the technique allows measurement of extremely thin surface films, providing a good estimation of the reaction rate.

This paper presents some examples of the application of electrochemical techniques to evaluate the environmental impact on the conservation of metallic artefacts in different French cultural institutions.

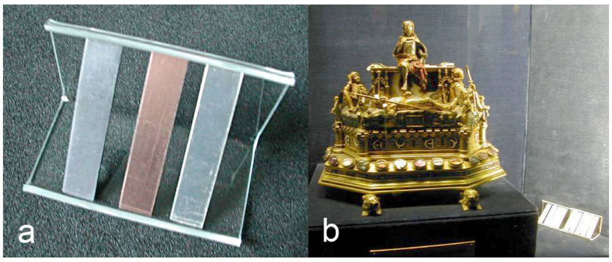

Figure 1. (a) The support structure for silver, copper and lead coupons; (b) The coupon assembly in a showcase.

Experimental

Three metallic sensors (commercial quality, Weber Métaux, Paris) have been used: sterling silver, copper and lead. Measuring 1 x 5 cm, they have been prepared by gently abrading both sides with a glass bristle, so that a homogeneous surface finish is obtained. To estimate the effect of particulate matter on the tarnishing reactions, a Plexiglas® support has been specially designed, so that coupons stay inclined at 45°, presenting one side faced up and the other down (Fig. 1a). Sets containing duplicate coupons of each metal have been placed in 15 cultural institutions, in storage and exhibition rooms, inside and outside display cases (Fig 1b).

A double-compartment cell described elsewhere [1] was used to analyse both sides of the coupons independently. Auxiliary electrodes were platinum wire (counter electrode) and mercury sulphate (MSE, reference electrode). Three different 0.1M solutions have been used as electrolyte: sodium citrate for silver, sodium acetate for copper and sodium sesquicarbonate for lead. Linear sweep voltammetry (LSV) was performed starting from open circuit value (OCP) towards negative values, until around -2VMSE.

Results

The extremely thin tarnish layers formed during exposure were hardly perceptible by eye, but could be easily detected upon electrochemical reduction, showing sharp current peaks. The potential value where each peak starts is characteristic of a given compound,

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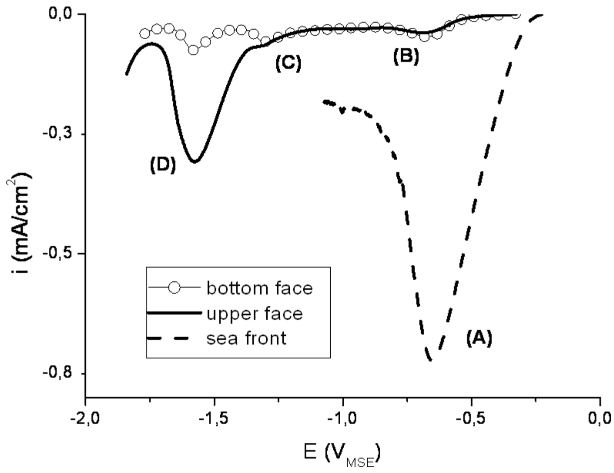

Figure 2. Typical reduction peaks recorded by reducing sterling silver surfaces in 0.1M sodium nitrate, after exposure in different environments.

and the area under the peak corresponds to the charge involved in that reaction, providing an estimate of the amount of product formed. Results shown here are from coupons collected after one year of exposure and summarize the main tendencies.

In the case of sterling silver, four different types of compounds could be identified, depending on the exposure location (Fig. 2). For the coupon kept outdoors, in a courtyard near the sea, a reduction peak starting at ca. -0.2 VMSE (A) can be assigned to silver chloride [1, 2]. Such a product was not found on coupons exposed in the rooms inside the museum, which present three other compounds: silver oxide, silver sulphide and a mixed silver-copper sulphide (reduction peaks B, C and D, respectively [3]. In such cases, comparison of curves recorded for each face of the same coupon shows a remarkably larger amount of this last compound on the upper face, indicating a probable selective corrosion induced by a deposit of particulate matter.

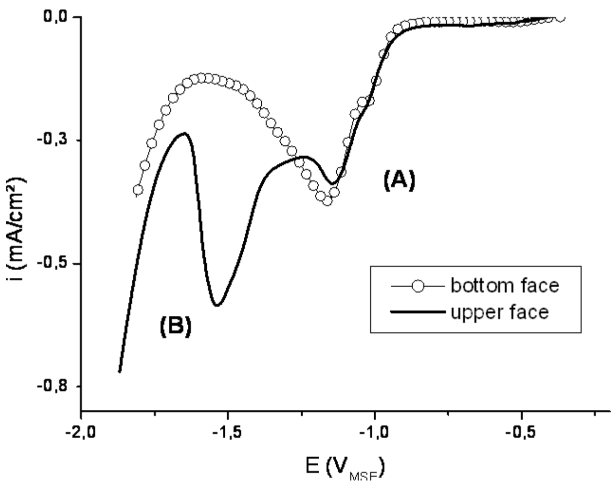

Figure 3. Typical reduction peaks recorded by reducing copper surfaces in 0.1M sodium acetate, after exposure in different environments.

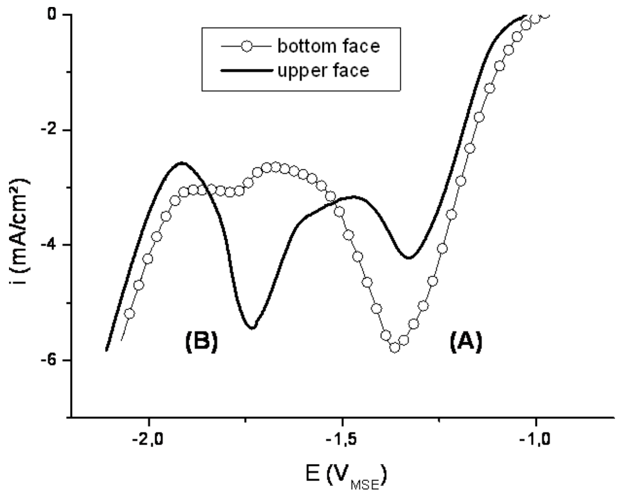

Figure 4. Typical reduction peaks recorded by reducing lead surfaces in 0.1M sodium sesquicarbonate, after exposure in different environments.

LSV performed on copper surfaces generally shows one or two current peaks: the one starting at ca. -0.9VMSE (A), was observed in all cases, while the more negative peak (B) is mostly observed for the upper face of the coupons [2, 4].

Finally, on lead, a similar general behaviour has been observed: a first broad reduction peak starting at ca. -1 VMSE (A), occurring for all coupons, and a second more negative peak (B), observable mostly on the upper side. This last peak was especially very large in wooden cupboards or display cases, and a complementary test confirmed a huge concentration of acetic acid [5], explaining the reactivity of lead.

The rate of tarnishing during the exposure period is estimated from the areas under the reduction peaks. The charge, which is proportional to the amount of material reacting, is shown in figure 5. Results are expressed as charge and not as loss of mass, since a precise identification of the corresponding compound was not possible [3].

Except in the case of lead exposed inside a display case containing high level of acetic acid, which has been found only in two particular situations, data shown in figure 5 are representative of the whole investigation: sterling silver was the less and lead the more reactive surface. Concerning silver coupons, it is worth noticing the high sensibility to particles deposited on the upper side. In fact, coupons exposed inside display cases don't present an important difference in tarnishing for each side, as is the case of those exposed in the room. In contrast, copper surfaces seem to be less sensitive to this effect, but present a general higher reaction rate. Lead is the most reactive of the three metals, certainly due to its natural tendency to form surface

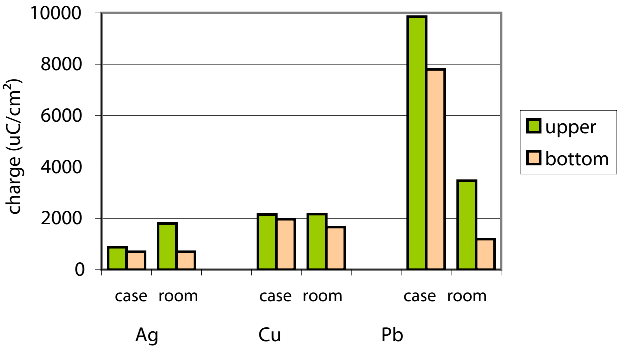

Figure 5. Calculated charge involved in the reduction reactions (approximately corresponding to the amount of compound formed during exposure) for specific situations. The lead values have been divided by ten.

films. Charges calculated on lead coupons are very high in all cases, and assume huge values in specific situations, like confinement inside a cupboard off-gassing organic acid.

The present results should be soon completed by the second measurement campaign, and the final conclusion will allow the definition of priorities concerning the purity of the environment.

Conclusions

It is possible to evaluate the environmental impact on metallic coupons using electrochemical techniques. Besides the fact that metals promptly react to their environment, expressing synergetic effects, the high sensitivity of the method allows a good qualitative and quantitative determination of surface compounds. The chemical nature of the compounds formed on sterling silver could be determined, supported by results obtained by grazing x-ray diffraction. For copper and lead, even though reduction peaks are sharp, it was not possible to identify the surface compounds.

The three metals react differently depending on the environment, but some general trends can be drawn. In all cases, the amount of product formed on the surface is smaller for coupons exposed inside showcases and for the underside of the coupon. This confirms the harmful effect of particulate matter, probably by absorbing humidity and catalyzing surface reactions. On the other hand, the protection provided by a showcase can be reversed if it contains harmful pollutants, as has been shown in the case of lead confined in cupboards in the presence of high concentrations of acetic acid.

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