



# Application of automated electrical resistance sensors for measurement of corrosion rate of copper, bronze and iron in model indoor atmospheres containing short-chain volatile carboxylic acids



Tomas Prosek<sup>a,\*</sup>, Michelle Taube<sup>b</sup>, Francois Dubois<sup>a</sup>, Dominique Thierry<sup>a</sup>

<sup>a</sup>Institut de la Corrosion/French Corrosion Institute, 220 rue Pierre Rivoalon, 29200 Brest, France

<sup>b</sup>The National Museum of Denmark, Dept. of Conservation and Natural Sciences, Brede, Denmark

## ARTICLE INFO

### Article history:

Received 27 February 2014

Accepted 14 June 2014

Available online 25 June 2014

### Keywords:

A. Copper

A. Bronze

A. Iron

C. Atmospheric corrosion

## ABSTRACT

The corrosion rate of copper and bronze Cu-8 wt.%Sn increased rapidly when the concentration of formic or acetic acid in air reached about 300 ppb at 80% relative humidity (RH) and a temperature of 20 °C. It decreased slowly during the several days after pollutant removal due to the slow rate of pollutant desorption from the metal surfaces. Corrosion of these metals was barely affected by the acids at RH up to 60%. For iron, the critical concentration of formic acid in air which led to surface activation at 80% RH was between 1000 and 1590 ppb.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Formic acid, HCOOH, and acetic acid, CH<sub>3</sub>COOH, are major corrosive pollutants in indoor cultural heritage premises. In contrast to sulphur dioxide, nitrogen dioxide and ozone, which come from external sources, they are of internal origin emitted primarily by wooden furniture [1–6]. Aside from the wood itself, carboxylic acids are released from the glues, adhesives, varnish and plastic accessories used regularly by the furniture industry [2,7]. Hardwoods, e.g. oak, beech and mahogany, are known to emit more acetic acid than softwoods due to a higher content of hemicellulose with acetyl group esters, which are prone to hydrolyse to acetic acid [3]. The emission of formic acid from wood is generally an order of magnitude lower than that of acetic acid, but still not negligible [3]. Other sources of carboxylic acids in museums and archives are hemicellulose-containing wrapping papers and cardboard [4], exhibited or stored objects made of wood, paper and some plastics [4,5], and conservation and preparation materials [7]. Smaller amounts of these pollutants may come from biogenic sources [1] and decomposition reactions, e.g., formaldehyde may decompose to formic acid upon adsorption on surfaces [2,7] and isoprene can be photo-oxidized to formic acid [8].

Typical concentrations of acetic acid in clean, low troposphere and urban areas are 0.1–2 and 0.2–8 ppb, respectively [9]. Due to

the numerous indoor sources of short-chain volatile carboxylic acids, their concentrations in rooms, showcases, storage facilities and cabinets usually exceed background outdoor levels. In indoor residences, concentrations of formic acid range from 9 to 33 ppb while those of acetic acid range from 9 to 88 ppb [10]. Allen and Miguel reported that exposure to acetic acid was enhanced 2–15 times indoors at different Brazilian sites [1]. Concentrations in hundreds or even thousands of ppb have repeatedly been reported in enclosures with limited air exchange in cultural heritage institutions [1,3,5,7,11–13]. When extreme values are excluded, concentrations of formic and acetic acid in indoor museum atmospheres range from low levels up to 500 and 2000 ppb, respectively.

Short-chain volatile carboxylic acids were reported to accelerate the degradation of objects made of lead [2–6], bronze and copper [3,5], zinc [4], iron [3], and glass [3] and to cause efflorescence on calcareous materials, such as shells, fossils, ceramics, pottery and limestone [3–5]. The deterioration of other materials such as paper or plastics can also be accelerated in their presence due to acidification [5]. Based on previous studies, recommendations on maximal concentrations of formic and acetic acids in indoor atmospheres were issued. The maximum average concentration of acetic acid for a 1- and 100-year preservation target for museum, gallery, library, and archival collections is set to 400 and 40 ppb, respectively, by the ASHRAE Handbook [9]. However, lower limits may be necessary for particularly sensitive materials such as lead.

Concentrations of short-chain volatile carboxylic acids in air can be measured using active or passive sampling techniques [5,11].

\* Corresponding author. Tel.: +33 298 058 905; fax: +33 298 050 894.

E-mail address: [tomas.prosek@institut-corrosion.fr](mailto:tomas.prosek@institut-corrosion.fr) (T. Prosek).

Passive sampling is more affordable; however, the results of an assessment are typically available only after a delay of several months following exposure of the samplers, transport and analysis in a specialized laboratory. In addition, the impact of carboxylic acids on material degradation is affected by a complex interplay among numerous factors such as temperature, relative humidity, the presence of other pollutants and ventilation patterns, which have not been fully investigated yet. Thus, it may be preferable to monitor their direct impact on materials of interest. This is traditionally done by exposing coupons of given materials to the environment and analysing their degradation after a certain exposure period. According to current standards and recommendations, a metal coupon needs to be exposed for 30 days or for 1 year [14–16]. The impact of the environment on metal degradation is then evaluated based on mass loss, mass gain or coulometric reduction of the corrosion products. The mass loss procedure is used for an assessment of outdoor corrosivity whereas mass gain is usually measured on coupons exposed indoors. The coulometric reduction of corrosion products is more demanding with respect to equipment and expertise but can provide an indication of the nature of the pollution in addition to the rate of metal degradation.

However, none of these techniques yields real-time data. Within the exposure period, valuable objects might further deteriorate if the air is contaminated. Since it is believed that information on the present corrosivity of the atmosphere is crucial to effective corrosion protection, an electronic logger, called AirCorr, which allows for continuous measurement of the corrosion rate of a metal in air has been developed [17,18]. The logger provides very high sensitivity enabling real-time corrosion monitoring even in low-corrosivity indoor facilities, good reproducibility for metals corroding mostly uniformly in a given environment, and good accuracy [19–23]. It makes use of the electrical resistance (ER) technique to monitor corrosivity. The use of ER is described in, e.g., ASTM standard G96 [24]. The concept 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. If the metal corrodes, the cross-sectional area of the track decreases and the electrical resistance increases. A part of the metal track is protected by an organic coating or tape and, thus, serves as a reference to compensate for resistivity changes due to temperature variations. Based on the initial cross-sectional area of the exposed element, the cumulative metal loss at the time of reading can be determined.

For a metal film with constant thickness corroding uniformly, the extent of corrosion can be represented as a corrosion depth. 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,  $\Delta h$ , can be calculated according to the equation

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

where  $h_{\text{ref,init}}$  is the initial thickness of the reference metallic track, which is assumed equal to the sensor track at the beginning of exposure;  $R_{\text{sens}}$  and  $R_{\text{ref}}$  are the current resistances of the sensor

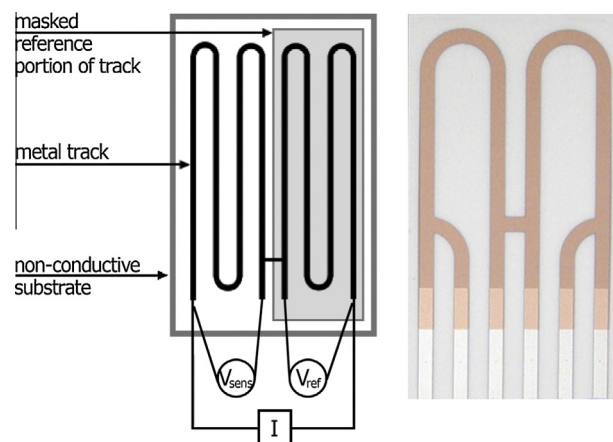


Fig. 1. Electrical resistance corrosion sensor; schematic drawing (left) and photograph of a 500-nm copper sensor (right).

and reference tracks; and  $R_{\text{sens,init}}$  and  $R_{\text{ref,init}}$  are the initial resistances of the sensor and reference tracks [20]. The calculation is based on the electrical resistance measured as a potential difference along the track through which a defined current passes.

Sensors made of the most technically important and some historical metal alloys in different thicknesses and sensitivities have also been developed [19,25]. A schematic drawing of a sensor is shown in Fig. 1 along with a photograph of one of the sensors without the reference part protection. The metal tracks were laid down by magnetron sputtering on a fine-grained  $\text{Al}_2\text{O}_3$  ceramic substrate [21]. The width of the measuring track is from 1 to 2 mm, depending on sensor type, and the length over 100 mm. This geometry ensures high sensitivity to changes in the electrical resistance due to metal corrosion.

For this study, the logger-sensor system was applied to monitor corrosion of copper, bronze and iron in model atmospheres containing controlled concentrations of formic and acetic acid at defined relative humidity and constant temperature. These systems have been studied by other researchers to determine the mechanism and kinetics of corrosion product formation on bulk metal [26–29]. For the thin-film copper, bronze, and iron sensors used in this study, the minimum detectable change in a metal track thickness due to corrosion was below 0.1 nm [19,20]. The main purpose of the work was to confirm the capability of the technique to assess small changes in air corrosivity in real time.

## 2. Experimental

### 2.1. Experimental chamber

A chamber allowing for corrosion studies in air with small and well-controlled concentrations of gaseous pollutants was built. It consists of an air dehumidifier, air filter, gas generator, humidifier, exposure chamber and exhaust air treatment unit. A schematic drawing of the system is shown in Fig. 2.

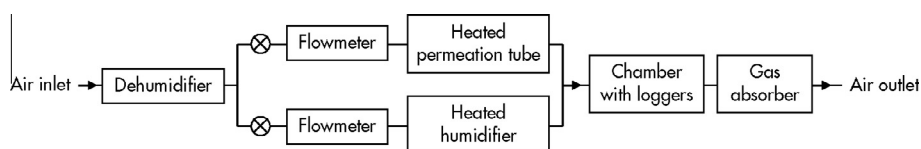


Fig. 2. Experimental setup for corrosion measurements in air polluted with carboxylic acids.

Download English Version:

<https://daneshyari.com/en/article/1468743>

Download Persian Version:

<https://daneshyari.com/article/1468743>

[Daneshyari.com](https://daneshyari.com)