

# Measurement Setup for the Development of Pre-Corroded Sensors for Metal Artwork Monitoring

M. Faifer<sup>1</sup>, S. Goidanich<sup>2</sup>, C. Laurano<sup>1</sup>, C. Petiti<sup>2</sup>, S. Toscani<sup>1</sup>, M. Zanoni<sup>1</sup>

<sup>1</sup>DEIB, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano (Italy)

<sup>2</sup>Chemistry, Materials and Chemical Engineering Department “Giulio Natta”, Piazza Leonardo da Vinci 32, 20133 Milano (Italy)

**Abstract** – The monitoring of environmental corrosivity towards cultural heritage is key task for both active and preventive conservation. In case of metallic artworks, this task can be performed by means of coupons or sensors realized with the same materials of the artworks to be conserved. In this work, a measurement system for the development and testing of sensor for atmospheric corrosivity monitoring is presented. The metrological features of the measurement system are analyzed aimed to the optimal analysis of a developed corrosion sensor. A sensor is also proposed. It permits to consider also the effect of the presence of corrosion layers on the object to be preserved, in order to achieve a better evaluation of its actual corrosion rate as a function of environmental conditions.

## I. INTRODUCTION

The real-time monitoring of cultural heritage is a very important task for the proper preservation of works of art. In particular metals may be highly sensitive to increases of relative humidity or to the presence of specific pollutants in the atmosphere. The monitoring of parameters such as humidity, temperature, pollutants etc. is a common practice [1], [2], that however do not provide specific information about the actual impact of the environment on the degradation rate of different materials. It is also possible to expose to the same environmental conditions the object to be monitored and a sample made with the same alloy. This approach permits performing also invasive measurement on the specimen without damaging the work of art [1], [3]-[5]. Another approach is the employment of environmental corrosivity sensors [6]-[10]. However, the most part of the sensor, do not consider the effect of the presence of corrosion layers over the surface. This is of particular importance when dealing with historic surfaces, which normally present quite complex stratigraphy of corrosion layers that can significantly affect their corrosion behavior [6], [10].

In order to implement a more effective tool for the monitoring of the degradation effects, pre-corroded sensors have to be developed and optimized. In a

preliminary work, the authors have developed a sensor that can be preliminary corroded so as to emulate the actual state of conservation of the artwork to be monitored [11]. The sensor is based on printed circuit board (PCB) technology and it requires a measurement system performing an electrical resistance tracking over the time. The optimization of the sensor and the study of corrosion processes require a vast laboratory activity supported by high accuracy measurements and controlled environment.

In this paper the developed measurement system and its metrological characterization will be presented. The system has been thought in order to guarantee high measurement performances, flexibility, modularity, good number of acquisition channel and easy use. The metrological characterization allowed to optimize the measurement system parameters so as to achieve the best performance.

A complete characterization including the effectiveness of the temperature compensation of the sensor thermal drift is here reported. The analysis has been performed on pre-corroded and not pre-corroded sensors.

## II. SENSOR DEVELOPEMENT

The development of the sensor has been driven by needs concerning cost, flexibility, exposed surface area, measurement system characteristics and sensitivity. In particular, the developed sensor had to guarantee:

- high surface area to be representative of real corrosion conditions,
- a proper distance between traces so as to avoid the presence of short circuit bridges due to the formation of corrosion products,
- possibility to be reconfigured by changing the sensor resistance value,
- allowing to perform a temperature compensation of the resistance variation due to temperature drift,
- low cost of production.

On the base of these constraints, a PCB solution has been adopted. The sensor has been designed in four sections, two for each face of the PCB to monitor different corrosion rates and implementing a temperature compensation as shown in Fig. 1. In this work terminal E

and E' have been connected in order to consider a full PCB face exposed to corrosion. One face will be protected from corrosion and will be adopted as reference for the temperature compensation ( $R_R$ ), while the other face is subjected to corrosion ( $R_C$ ). The sensor geometrical parameters have been chosen as shown in Fig. 1. Tracks have been realized in copper with a thickness of  $17 \mu\text{m}$  so that each face of the sensor has a nominal value of  $0.317 \Omega$ .

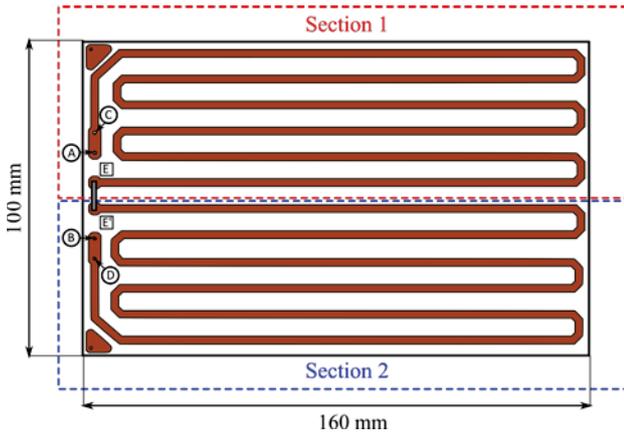


Fig. 1. Sensor layout.

In the preliminary design phase, different environmental conditions leading to corrosion rates ranging from  $10^3 \mu\text{m}/\text{year}$  (representing highly polluted and aggressive outdoor environment) to  $5 \cdot 10^{-3} \mu\text{m}/\text{year}$  (representing controlled environment with low levels of RH and pollutants) have been considered.

The corrosion rate ( $\mu\text{m}/\text{year}$ ) is defined by assuming that corrosion is uniform on the sensor surface. This means that only the thickness of the sensor is ideally involved in the corrosion process. Now, let us consider the expression of the resistance in terms of resistivity  $\rho$  and geometrical parameters:

$$R = \rho \frac{L}{S} = \rho \frac{L}{h\delta} \quad (1)$$

where,  $L$ ,  $h$ ,  $\delta$  are respectively the total length, the width and the thickness of the PCB tracks. Therefore, there is an inversely proportional relation between the resistance of the sensor and its thickness. Therefore, by monitoring the variation of the sensor resistance it is possible to obtain information also about the corrosion rate. Moreover, it is clear that the choice of track thickness directly affects the lifetime of the sensors. The design of the sensor has been optimized in terms of lifetime and sensitivity for a specified level of corrosion rate, within a reasonable range of variation.

Measuring  $R_R$  and  $R_C$ , it is possible to compensate the thermal drift of the resistance by computing the ratio between the two faces of the sensor resistances for a generic temperature  $T$ :

$$K_C = \frac{R_C}{R_R} = \frac{R_{C0}(1 + \alpha(T - T_0))}{R_{R0}(1 + \alpha(T - T_0))} = \frac{R_{C0}}{R_{R0}} \quad (2)$$

where  $R_{C0}$  and  $R_{R0}$  are the corrosion and reference resistances at the temperature  $T_0$  while  $\alpha$  is the thermal coefficient of the conductive material of the PCB tracks.

Assuming that the corrosion acts uniformly on the PCB tracks only on  $R_C$ , it is possible to define the relative variation of the thickness between a generic time  $t$  and a reference time  $t_0$  of  $R_C$ :

$$\gamma = \frac{\delta_C(t_0) - \delta_C(t)}{\delta_C(t_0)} \quad (3)$$

Therefore,  $K_C$  at the generic time  $t$  is defined as

$$K_C(t) = \frac{L_C}{h_C \delta_C(t_0)(1 - \gamma(t))} \frac{h_R \delta_R}{L_R} \quad (4)$$

where  $\gamma(t)$  is the relative reduction of the track thickness. By normalizing  $K_C(t)$  with respect to its value at the reference time  $t_0$ , it is possible to estimate the variation of the thicknesses and hence the corrosion rate:

$$C(t) = \frac{K_C(t)}{K_C(t_0)} = \frac{R_C(t) R_R(t_0)}{R_R(t) R_C(t_0)} = \frac{1}{1 - \gamma(t)} \quad (5)$$

In this way, by monitoring the value of the ratio  $C(t)$  it is possible to quantify the corrosion rate. Naturally, the minimum detectable variation of  $C(t)$  strongly depends on the resolution of the instrument used to perform the resistance measurements.

### III. MEASUREMENT SETUP

In order to properly characterize the proposed sensor a VI-based measurement system has been developed (Fig. 2). The measurement setup has to guarantee good measurement performances, flexibility, modularity, good number of acquisition channels and easy use.

A Keithley 3706 has been used for performing the required 4-wires resistance measurements. In this way, no contact resistances are included in the resistance measurement. This instrument has been chosen as it provides a multi-channel measurement solution by means of switching cards. In this way, different pre-corroded sensors can be tested with the same high-resolution digital multi-meter (DMM) with a cost-effective solution. In fact, each switching card can perform 20 4-wire resistance measurements. The Keithley 3706 owns six slots, so that potentially 120 resistance measurements can be acquired with one DMM. In this work only one switching card has been connected.

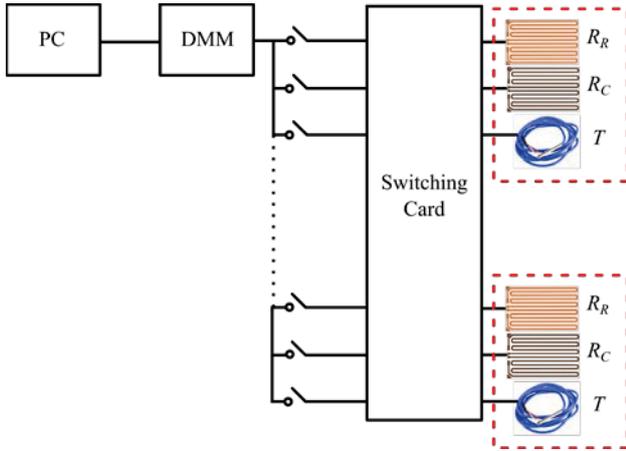


Fig. 2. Measurement system architecture.

For each tested sensor, three resistance measures are required: the resistance of the track exposed to corrosion, the resistance of the track used as reference for the temperature compensation and the resistance of the pt100 temperature sensor. Given this requirement, the measuring system is able to accommodate 6 sensors for their characterization.

Every single measure is the results of 10 averaged measures performed over 5PLC. The minimum analysis time for each sensor is 18s. These limits and configuration parameters have been defined on the base of a measuring system characterization that is reported in the following section.

For each measure the mean value and its standard deviation are computed and saved on a log file. The interface of the developed measuring system is reported in Fig. 3. The interface is made up of a configuration panel allowing setting the instrument parameters and a measurement panel on which the measurements over time of the three resistances are shown.

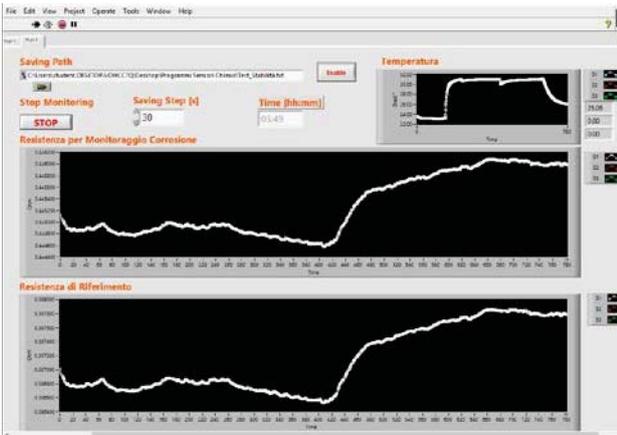


Fig. 3. VI front panel.

#### IV. MEASUREMENT SYSTEM CHARACTERIZATION

In order to evaluate the accuracy and the sensitivity of the measurement system a series of test have been performed. First, the measurement noise of the system has been evaluated by performing a measurement campaign on a standard resistance  $R_S=0.1 \Omega$  characterized by low thermal coefficient and placed into a climatic chamber guaranteeing a temperature of  $23.0 \text{ }^\circ\text{C} \pm 0.2 \text{ }^\circ\text{C}$ . The temperature has been monitored by means of a digital thermometer Dostman Electronics modell P655-LOG with Pt100 sensor. In the meanwhile, a second channel has been used for measuring the resistance of one face of the developed sensor placed in the same climatic chamber. Referring to Fig. 1, the current was injected from terminal A and collected at terminal B while the voltage drop was measured between terminals C and D. This allows to evaluate the noise related to the sensor geometry and connections. The experimental setup has been reported in Fig. 4.

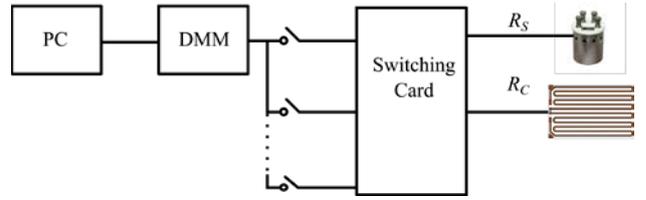


Fig. 4. Measurement system characterization setup.

The DMM range has been set to  $1 \Omega$ , suitable for both the standard resistance and the developed sensor. Dry circuit and offset compensation features have been enabled. The DMM in 4-wire resistance configuration allows setting the measurement time in terms of Number of Power Line Cycle (NPLC).

Moreover, the time between the closing operation of the switching card and the DMM activation can be controlled; this intentional delay time  $T_D$  can be used to ensure that the resistance measurements are performed when the system is in steady state condition.

In order to optimize the DMM parameters, different tests have been performed on the standard and the sensor resistances.  $N=100$  measurements for both channels have been performed ranging  $T_D$  from 0 to 10 s and considering NPLC equal to 1, 5, 10. For each channel acquired in each test condition, the measurement noise has been estimated as the sample variance over the  $N$  measurement:

$$s(R) = \sqrt{\frac{1}{N-1} \sum_{n=1}^N |R^{[n]} - R_{\text{avg}}|^2} \quad (6)$$

The standard deviation has been performed for both the standard resistance  $R_S$  and the sensor resistance  $R_C$  on the  $N$  measurements. Results have been reported in Fig. 5 and Fig. 6 respectively for different  $T_D$  and NPLC.

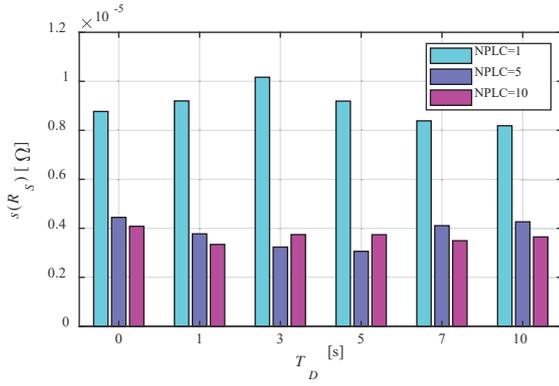


Fig. 5. Standard deviation of  $R_S$  in different test conditions.

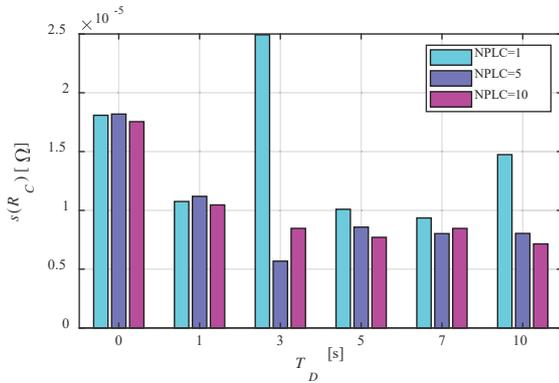


Fig. 6. Standard deviation of sensor resistance in different test conditions.

Focusing on the standard deviation of  $R_S$ , it can be highlighted that when NPLC=1 is considered, the overall uncertainty is much higher than those with NPLC=5 and 10 setting (approximately the double). When no  $T_D$  is considered, a higher value of standard deviation is noted. Therefore, it can be stated that best trade-off between measurement time and uncertainty is obtained for NPLC=5, as expected also from the datasheet of the instrument [12]. By moving to the sensor resistance  $R_C$ , higher values of standard deviation in all the cases are recorded but the same trend is highlighted.

So, for each  $T_D$ , best results are achieved with NPLC=5. In fact, passing to NPLC=10, namely doubling the observation time, no considerable improvements in terms of standard deviation are achieved.

Focusing on data for NPLC=5, it is necessary to check if measurements of resistances have been performed in steady state condition for each  $T_D$ . For this reason, measurements of the resistances have been reported in Fig. 7 and Fig. 8 for the standard and the sensor resistances respectively.

Focusing on the standard resistance  $R_S$ , it can be highlighted that when no delay is set, there is a transient effect that lasts about 10 measurement points. By increasing  $T_D$ , this transient effect is mitigated. On the

other hand, considering the sensor resistance  $R_C$ , this behavior is more evident: at least  $T_D = 3$  s has to be considered for neglecting the transient effects. Differences on the dynamic behavior can be attributed to different impedance of two channels.

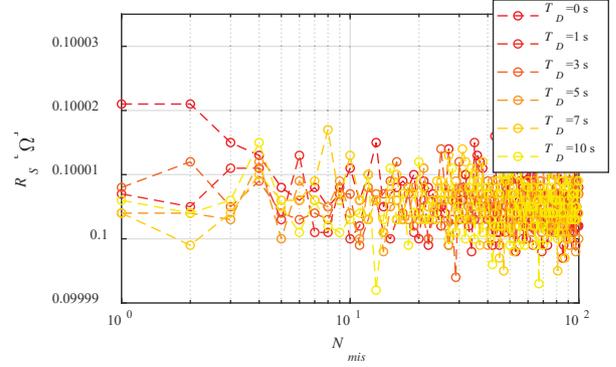


Fig. 7. Measurements of  $R_S$  for NPLC=5 and different  $T_D$ .

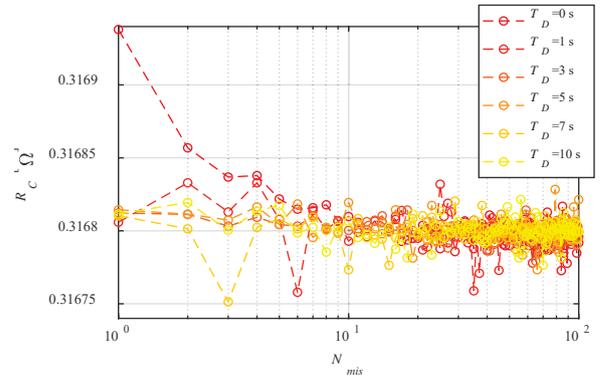


Fig. 8. Measurements of  $R_C$  for NPLC=5 and different  $T_D$ .

Finally, it is possible to declare that the best trade off in terms of accuracy and time is achieved with  $T_D=5$  s and NPLC=5; in these conditions the standard deviation on the standard resistance reaches a value of  $3.7 \cdot 10^{-6} \Omega$  while for the sensor resistance reaches a value of  $8.7 \cdot 10^{-6} \Omega$ . This difference can be attributed to the design of the PCB sensor and other environmental noise sources. As a final point on the measurement noise analysis, the standard uncertainty has to be referred to the average value of  $R_C$  on the all 100 measurements:

$$u_A(R_C) = s(R_{C,avg}) = \frac{s(R_C)}{\sqrt{N}} \quad (7)$$

that results  $8.7 \cdot 10^{-7} \Omega$ .

## V. EXPERIMENTAL RESULTS

The presented measurement system has been developed to monitor the effect of different environmental conditions on the corrosion behavior of the developed sensors. As aforementioned one face of each sensor has been protected from the environment by means of three layers of Inralac. In particular, the preliminary measurement

campaign has been performed considering 4 sensors: one was not pre-corroded (S03); on S01 a layer of Cuprite ( $\text{Cu}_2\text{O}$ ) was realized, while on S02 and S04 a chloride and sulfate-based patina was formed. The aim was to produce representative artificial patinas of the composition of a series of corrosion products commonly found on the surfaces of cultural heritage objects. The cuprite patina was selected because it is the first corrosion product that normally forms on copper alloys. The chloride and sulfate-based patina was instead selected in order to reproduce the surface conditions of highly unstable artefacts from a corrosion point of view.

Before considering performance of the developed sensor in the corrosion monitoring, it is crucial to verify the efficiency of the temperature compensation in different corrosion condition of the sensors. The sensors have been placed in a climatic chamber. RH was kept below 20% in order to have negligible corrosion rates. A temperature profile has been set and monitored by means of a pt100. Temperature measurement has been reported in Fig. 9

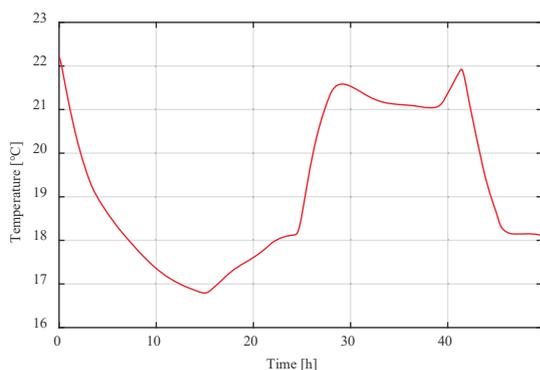


Fig. 9. Temperature over time.

The developed measurement system has acquired data for 48 hours for sensors S01, S02, S03 and S04.  $C(t)$  has been computed for each sensor as shown in (5). Results have been reported in Fig. 10.

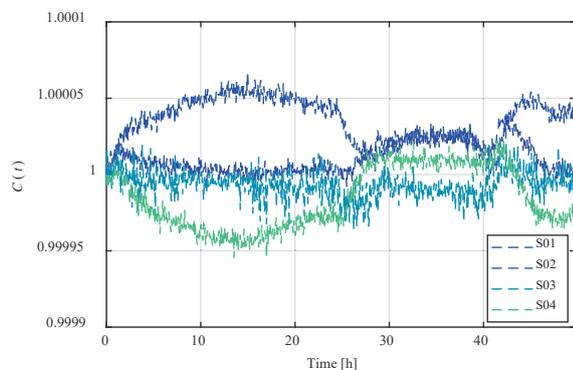


Fig. 10.  $C(t)$  over time for sensor S01, S02, S03 and S04.

Experimental results show that the performed temperature compensation achieves good performance. In fact, if S02 and S03 are considered the fluctuation of  $C(t)$  are on the order of 0.005% while for S01 and S04 are lower. This means that corrosion producing a variation on  $C(t)$  higher than this value can be attributed to the corrosion effects in the considered temperature range.

## VI. CONCLUSION

In this paper, the metrological characterization of a system allowing monitoring the environmental corrosivity towards copper-based sensors has been presented. Moreover, a sensor allowing to track the corrosion behavior considering the presence of corrosion layers over historic surfaces has been presented. The measuring system is characterized by flexibility, modularity and it permits to perform measurements on up to 40 sensors. On the base of preliminary tests, the system seems to be very promising. In particular the measurement uncertainty due to the measurement system and the temperature compensation process has been evaluated. The achieved accuracy permits to monitor corrosion sensors for heritage preservation. The developed system can be considered a good solution for the development and characterization of sensors for metal work of art monitoring.

## REFERENCES

- [1] M.La Gennusa, G.Rizzo, G.Scaccianoce, F. Nicoletti, "Control of indoor environments in heritage buildings: experimental measurements in an old Italian museum and proposal of a methodology," *Journal of Cultural Heritage*, vol. 6, 2005, pp. 147-155.
- [2] D.De la Fuente, J.M.Vega, F.Viejo, I.Díaz, M.Morcillo, "Mapping air pollution effects on atmospheric degradation of cultural heritage," *Journal of Cultural Heritage*, vol. 14, 2103, pp. 138-145.
- [3] G.M.Ingo, E.Angelini, C.Riccucci, T.De Caro, A.Mezzi, F.Faraldi, D.Caschera, C.Giuliani, G.Di Carlo, "Indoor environmental corrosion of Ag-based alloys in the Egyptian Museum (Cairo, Egypt)," *Applied Surface Science*, vol. 326, 2015, pp. 222-235.
- [4] M.Ryhl-Svendsen, "Corrosivity measurements of indoor museum environments using lead coupons as dosimeters," *Journal of Cultural Heritage*, vol 9, No.3, 2008, pp. 285-293.
- [5] D.Thickett, R.Chisholm, P.Lankester, "Reactivity Monitoring of Atmospheres", *Metal 2013 - Interim Meeting of the ICOM-CC Metal Working Group*. 2013, Edinburgh, Scotland.
- [6] S.Goidanich, D.Gulotta, L.Brambilla, R.Beltrami, P.Fermo, L.Toniolo, "Setup of galvanic sensors for the monitoring of gilded bronzes," *Sensors*, vol. 14,

No.4, 2014, pp. 7066-7083.

- [7] L.Sjögren, N.L.Bozec, "On-line corrosion monitoring of indoor atmospheres," in EUROCORR 2004, Nice, France.
- [8] T.Prosek et al., "Real-time monitoring of indoor air corrosivity in cultural heritage institutions with metallic electrical resistance sensors," Studies in Conservation, vol 58, 2013, pp. 117-128.
- [9] H.Agbotu et al., "Remote assessment of cultural heritage environments with wireless sensor array networks," Sensors 2014, vol. 14, No.5, pp. 8779-8793.
- [10] J.P.Dracott, "Piezoelectric printing and pre-corrosion: Electrical Resistance Corrosion Monitors for the conservation of heritage iron," in Faculty of Engineering and Physical Sciences, 2014, University of Manchester, Manchester.
- [11] C. Petiti, M. Faifer, M. Zanoni, S. Goidanich, "Based Sensors for Monitoring Atmospheric Corrosivity on Corroded or Patinated Copper-Based Objects," METAL 2019, Proceedings of the Interim Meeting of the ICOM-CC Working Group on Training in Conservation and Restoration, 2-6 September 2019, Neuchâtel, Switzerland.
- [12] [https://download.tek.com/manual/3700AS-901-01C\\_Jul\\_2016\\_Ref\\_3.pdf](https://download.tek.com/manual/3700AS-901-01C_Jul_2016_Ref_3.pdf)