

Monitoring Corrosion Products on Metal Artefacts by Linear Sweep Voltammetry (LSV)

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Metallic surfaces are highly sensitive to their surroundings, and prone to react with airborne pollutants to form complex layers. Electrochemical techniques have the possibility of simultaneously identifying different electroactive compounds [1]. The high sensitivity of Linear Sweep Voltammetry (LSV) allows the detection of extremely thin surface films before they became visible. LSV leads to reduction peaks, which can identify the compounds within the “tarnishing” layer and also its relative abundance [1, 2]. The potentialities of this and others electrochemical techniques has been well demonstrated in several recent works and they seem to be promising and non-invasive tools, even for in situ investigations on the metallic artifacts from cultural heritage.

This communication presents data showing the application of the technique to silver and sterling silver coupons exposed, during periods of 1 and 12 months, in the Treasure Room in the Museum (inside showcases) and near the Holy Altar of the Chapel, of Porto Cathedral (Portugal). The influence of various conditions: the atmosphere (Museum and Chapel), exposure time (1 and 12 months) and season (spring, summer, autumn and winter) have been analysed. The LSV spectra of blank polished samples as well as samples covered with thin films of silver sulphide and of silver chloride, formed under controlled conditions, respectively: (i) H₂S, 1000 ppm, RH= 53% ± 2, T= 21 °C ± 1, over periods of 24, 48 and 72 h) and (ii) 3.5% of NaCl, RH=41% periods of 5 h, have been used as references.

Concerning the nature of the products developed on the surface during the exposure, data has revealed that the tarnishing layers have a complex nature and are not composed only by silver sulphide. It happens even that silver sulphide is a relative minor component in the tarnish layer. Peaks corresponding to silver chloride and silver oxides were well visible. Small peaks assigned to silver sulphide were identified on the samples exposed in the Chapel. For the 12 months exposures both peaks have increased in size with the peak assigned to chloride being much higher in the case of the Chapel. The seasonal influence, even for the 1 month exposures, was particularly notable on those samples with exposures started in winter with well visible effects on the chloride peak on the tarnish layer of the samples exposed in the Chapel.

Obviously, that to obtain analytical information electrochemical techniques can be complemented with spectroscopic techniques, namely, X- ray photon spectroscopy (XPS), laser induced breakdown spectroscopy (LIBS), x-rays fluorescence spectroscopy, among others.

[1] A. Doménech-Carbó, M.T. Doménech-Carbó, V. Costa (2009), *Electrochemical Methods in Archaeometry, Conservation and Restoration*, Berlin: F. Scholz.

[2] V. Costa, M. Dubus (2007), Impact of the environmental conditions on the conservation of metal artifacts: an evaluation using electrochemical techniques, in National Museum of Denmark, *Museum Microclimates*, Copenhagen: T. Padfield and K. Borchersen, 63-65.