Controlling pollution effects on metallic cultural heritage using linear sweep voltammetry

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AIMS

Linear Sweep Voltammetry (LSV) is a technique that allows the identification of the constituents of the thin tarnishing layers and its relative abundance [1, 2]. Minor amounts of the main compounds formed on the tarnish layer on silver and silver alloy samples exposed in the museum and in the chapel of Porto Cathedral, in Portugal, have been identified.

Tarnishing process and atmospheric pollutants

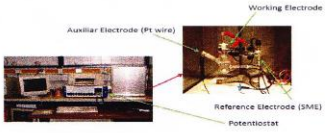
The tarnish process of silver and silver alloys is strongly dependent on the nature and levels of pollutants and on the climatic parameters such as: relative humidity (RH), average temperature, winds direction and intensity, etc.

In spite of the amount of studies the tarnishing process of silver and silver alloys under natural atmospheres is not completely understood.

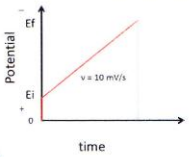
According to Graedel et al [3] hydrogen sulfide (H_2S) and carbonyl sulfide (OCS) are the principal atmospheric aggressive gases for silver and copper leading to silver sulfide, however it is well documented in the literature that the formation of sulfides requires a minimum level of H_2S.

Others such as Hallett et al [4] have identified the presence of several species other than silver sulfide.

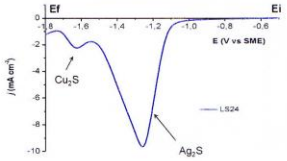
EXPERIMENTAL



Linear Sweep Voltammetric Potential Profile



Cathodic Spectra



Working electrodes (made with exposed and non exposed samples)

Reference Samples

Ag (**P**) & Ag:Cu (**L**)

- Polished samples (blanks) — **PB & LB**
- exposed to a chloride controlled atmosphere - **PCl & LCl** (3.5 % NaCl, RH=41%, T=43 ºC, 5 h)
- exposed to H_2S atmosphere – **PS24, PS48, PS72 & LS24, LS48 and LS72** (H_2S 1000 ppm; RH=53%; T=21 ºC; t_{exp} =24, 48 ,72 h)

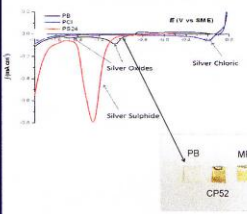
Exposed Samples

Ag (**P**) & Ag:Cu (**L**)

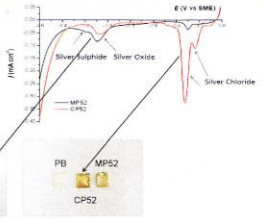
- Chapel (**C**)
  - **1 month**: starting in **Spring** (CP4Sp, CL4Sp), **Summer** (CP4S, CL4S), **Autumn** (CP4A, CL4A), **Winter** (CP4W, CL4W)
  - **12 months**: starting in Spring (CP52, CL52)
- Museum (**M**)
  - **1 month**: starting in **Spring** (MP4Sp, ML4Sp), **Summer** (MP4S, ML4S), **Autumn** (MP4A, ML4A), **Winter** (MP4W, ML4W)
  - **12 months**: starting in Spring (MP52, ML52)

RESULTS

LSVs of reference samples

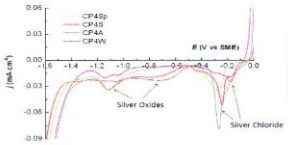


LSVs revealing the effect of exposure time

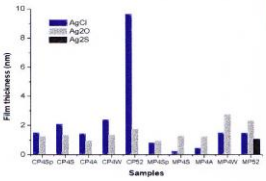


Up & Down at 45°

Seasonal influence



Estimated film thickness



CONCLUSIONS

LSV has identified as main components on all the samples as being silver chloride and silver oxides and only in a few samples silver sulfide and a mixed copper-silver sulfide. Film thicknesses ranging between 0.22 and 9.63 nm were estimated.

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