Patinas on silverwork
Analytical approach for distinguishing intentionally and naturally corroded surfaces

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INTRODUCTION

The patination of silverwork to modify surface color and finish became increasingly popular in 19th-century Europe, particularly among renowned artists such as René Lalique (1860-1945), Henri Vever (1854–1942), and Georges Fouquet (1862–1957). This decorative technique is typically achieved using sulfur-based solutions, resulting in blackish or bluish silver sulfide patinas[1].

Patinated silver surfaces often exhibit a characteristic glossy finish, while environmental degradation typically results in a dull, matte appearance, creating visually heterogeneous surfaces that require conservation actions (Fig. 1). However, the chemical similarity between artificial patinas and naturally formed corrosion layers presents a significant challenge - Selecting a cleaning approach that effectively removes the natural corrosion without damaging the original decorative surface[2].

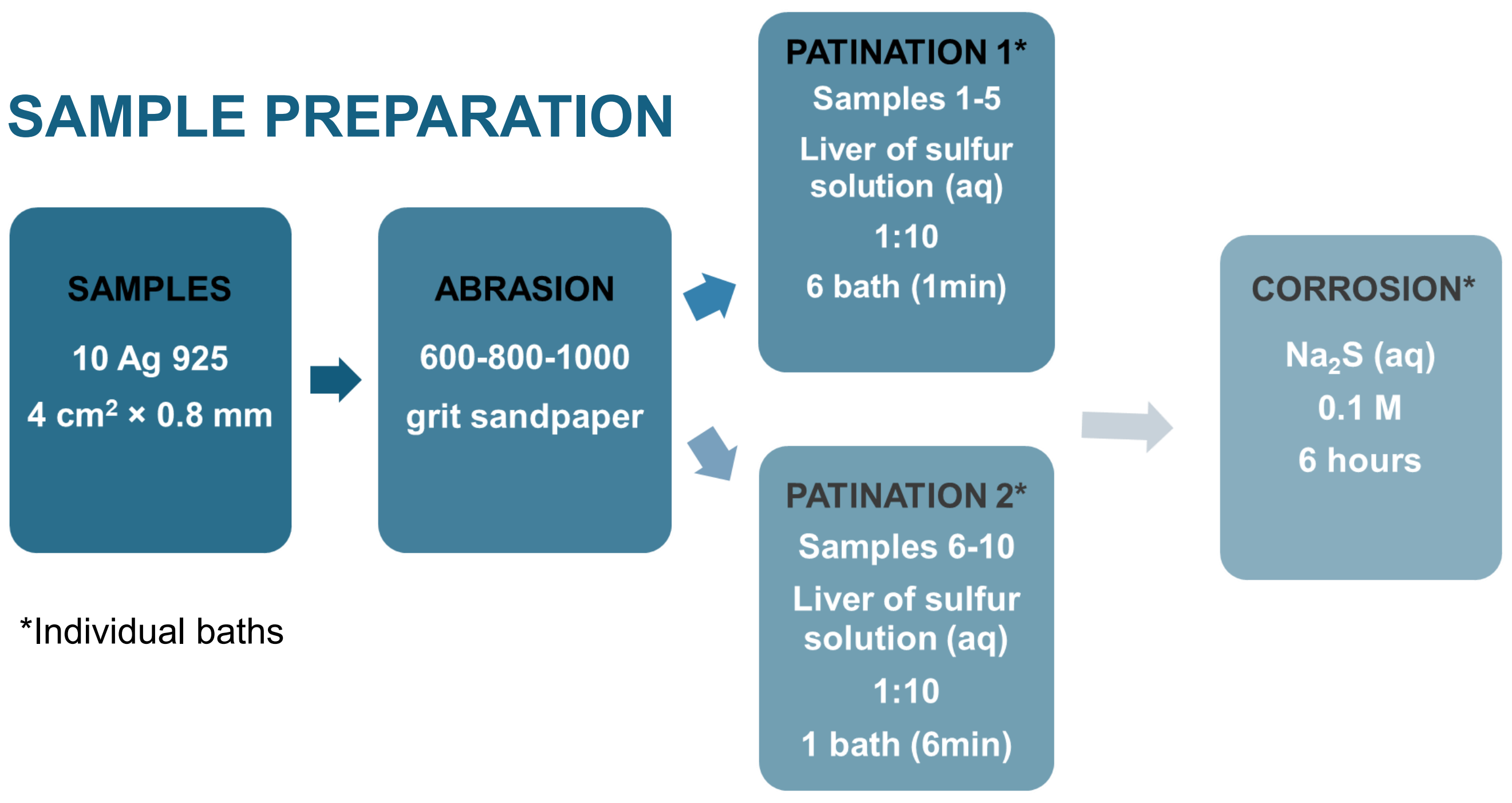
Fig. 1 - René Lalique, sugar bowl *Snakes* , c. 1897-1900. Patinated silver and blow glass. Museum Calouste Gulbenkian©.

RESEARCH FOCUS

Develop an analytical methodology based on the optical properties of patinated and naturally corroded silver, to support conservation cleaning actions that selectively remove corrosion while preserving the original decorative patinated finish.

METHODOLOGY

SAMPLE PREPARATION



SAMPLES
10 Ag 925
4 cm² × 0.8 mm

ABRASION
600-800-1000 grit sandpaper

PATINATION 1*
Samples 1-5
Liver of sulfur solution (aq)
1:10
6 bath (1min)

PATINATION 2*
Samples 6-10
Liver of sulfur solution (aq)
1:10
1 bath (6min)

CORROSION*
Na_2S (aq)
0.1 M
6 hours

*Individual baths

SURFACE CHARACTERIZATION

To characterize the optical and morphological changes, reflectance in the visible spectrum and CIE *Lab* color parameters were measured before and after corrosion. Additionally, scanning electron microscopy (SEM) was used to characterize the surface morphology.

RESULTS AND DISCUSSION

REFLECTANCE

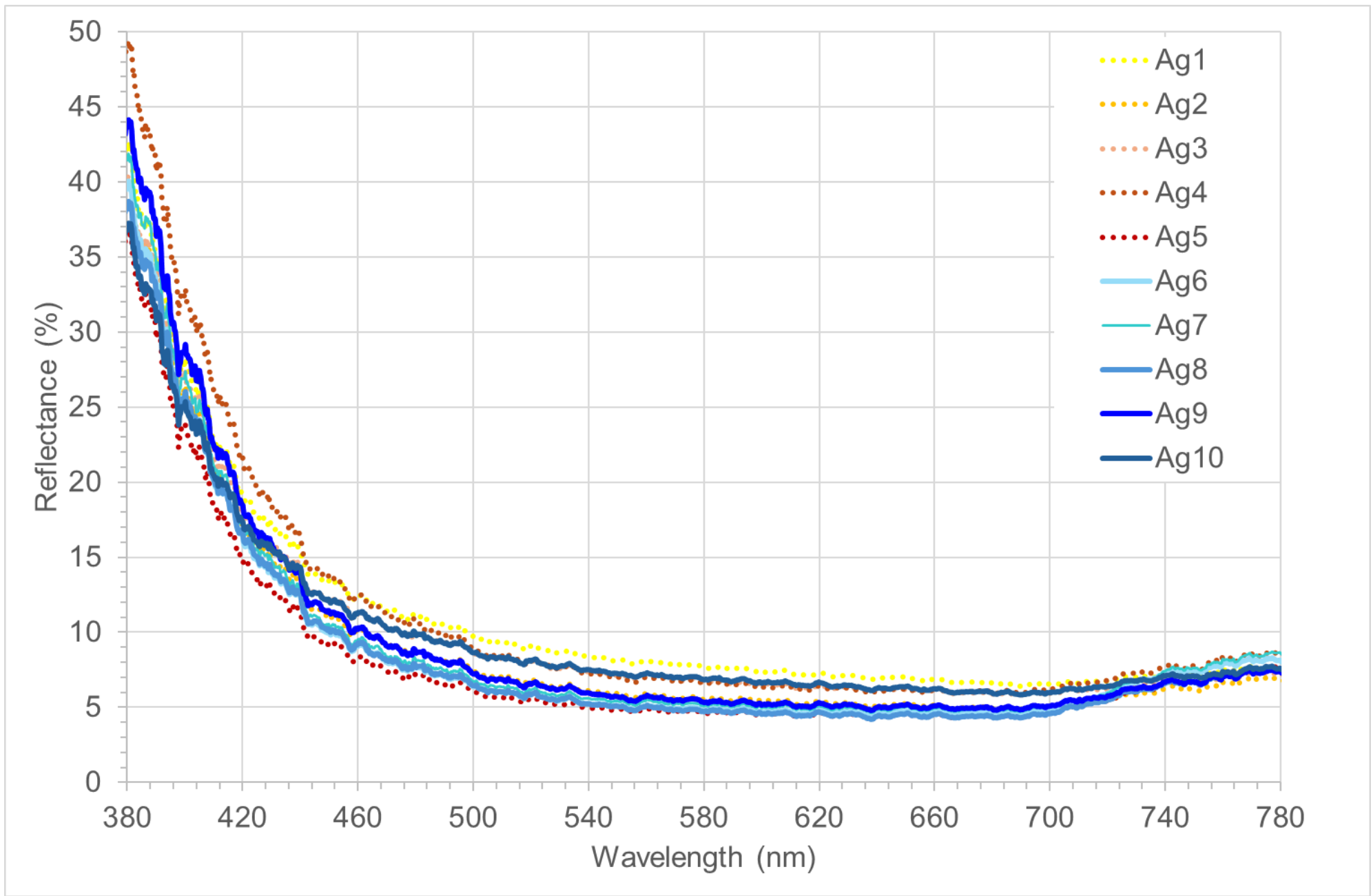


Fig. 3 – Reflectance spectra of silver patinated samples showing similar results across both patination procedures.

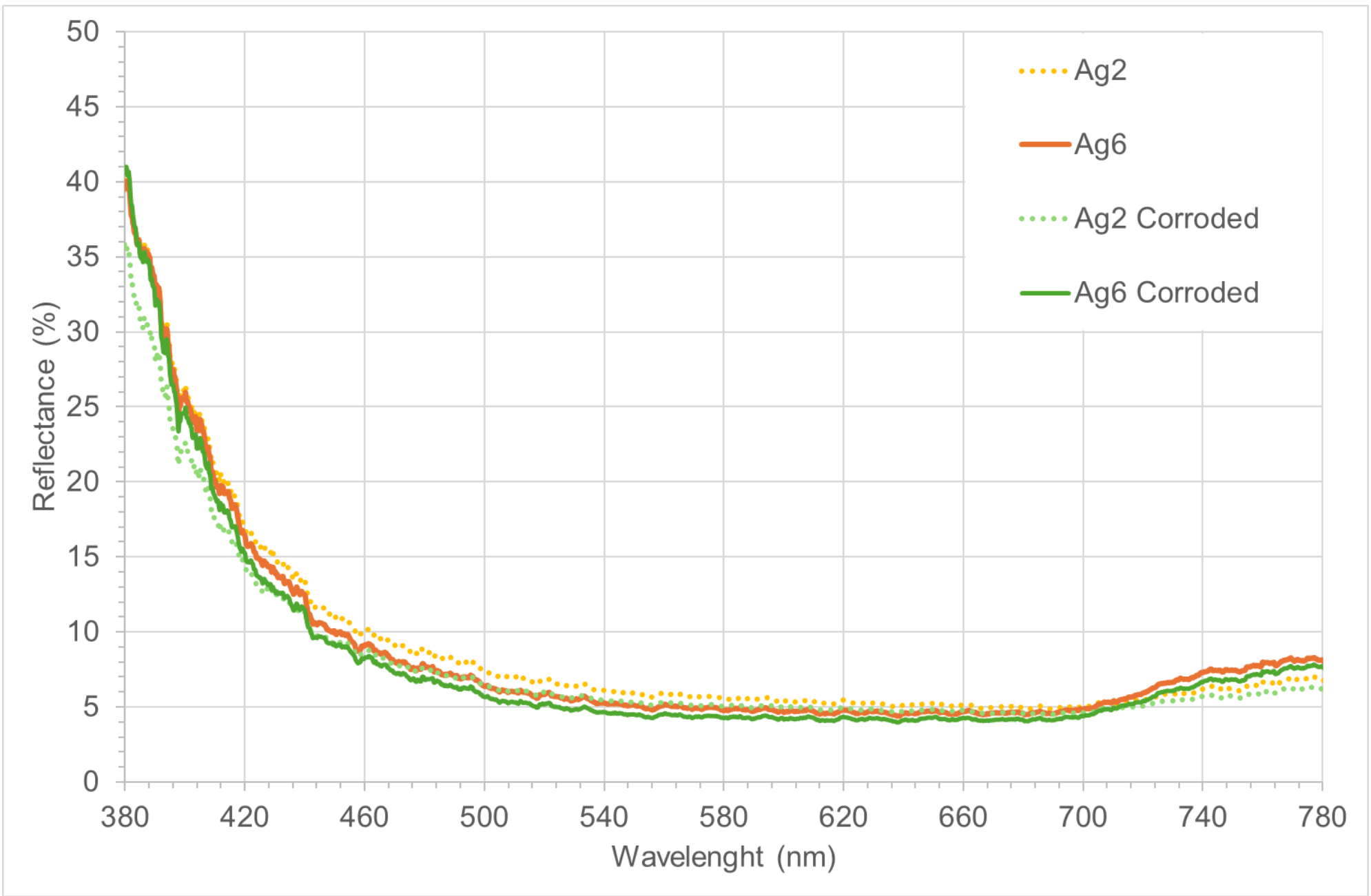


Fig. 4 – Reflectance spectra of silver patinated samples before and after corrosion, showing similar results for both surface types.

COLORIMETRY

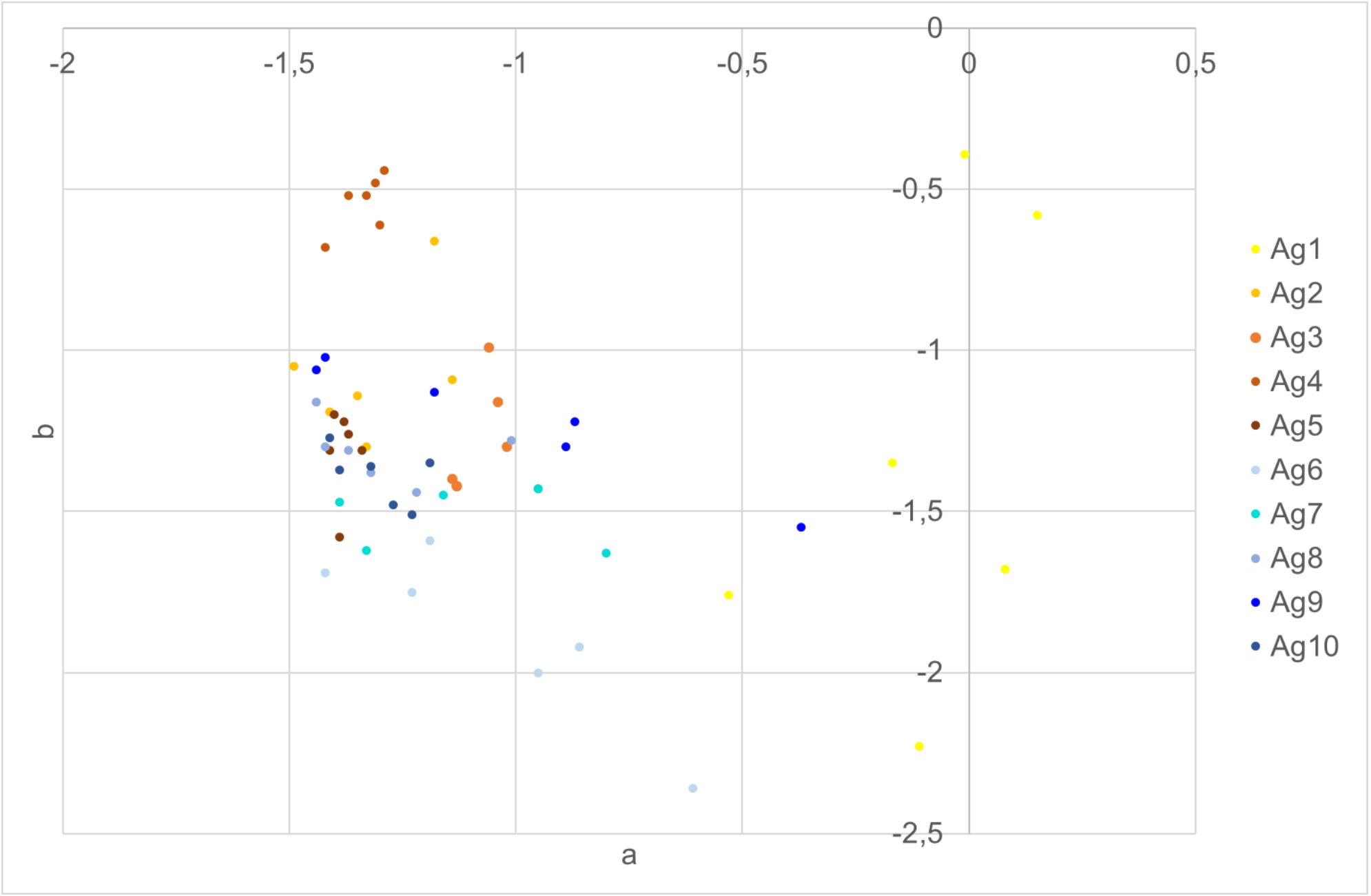


Fig. 5 – Colorimetry data for silver samples subjected to different patination procedures. Although the CIE *a* and *b* parameters do not provide a clear distinction between different patination, measurable differences exist. CIE *L* is around 50 for all samples.

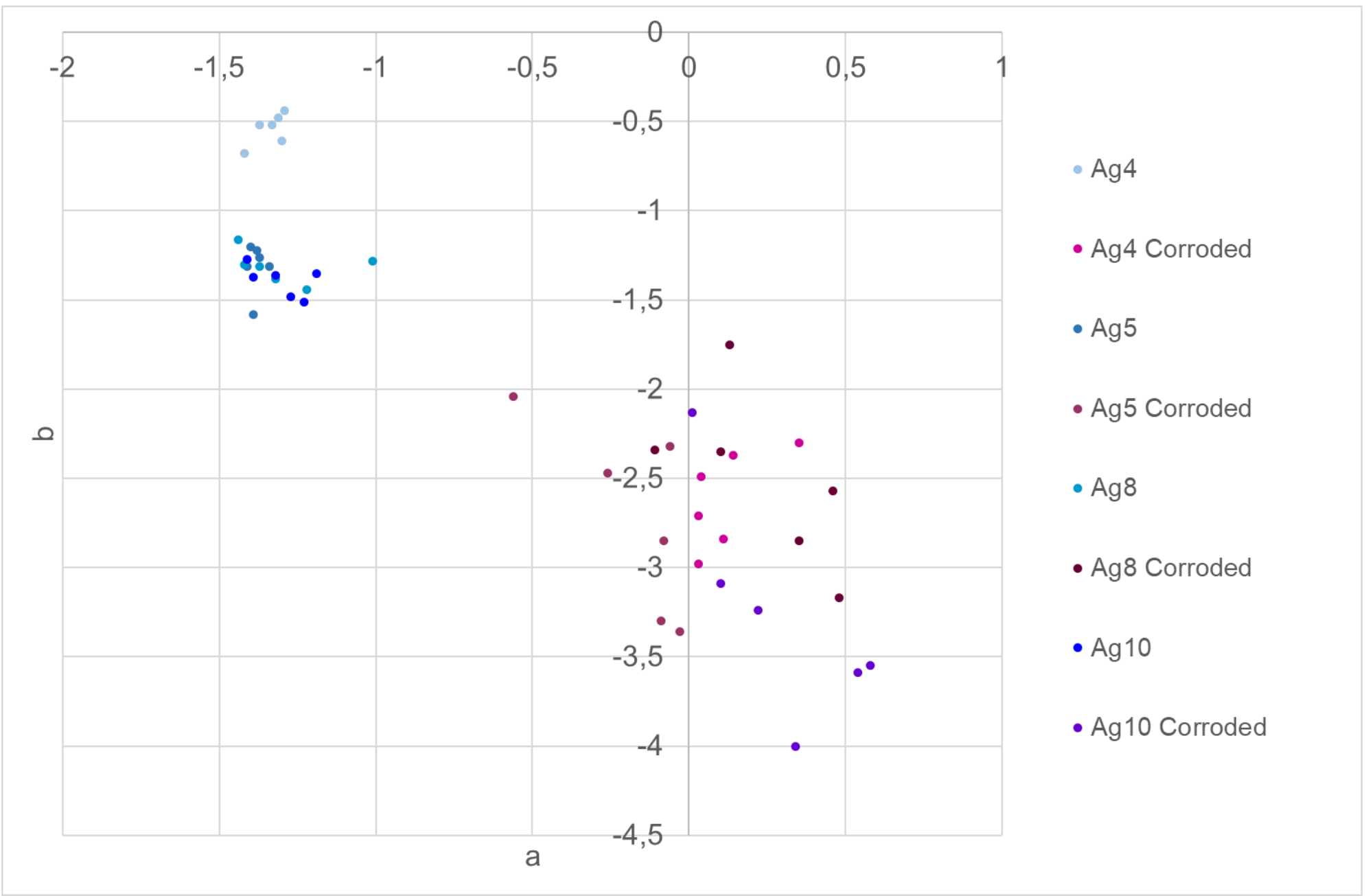


Fig. 6 – Colorimetry data for silver patinated samples before and after corrosion. The CIE *a* and *b* parameters show a clear distinction between surface types: non corroded patinas typically exhibit a < 0 while corroded patinas often shift toward a > 0 (Fig. 6). CIE *L* is around 50 for all samples.

SCANNING ELECTRON MICROSCOPY

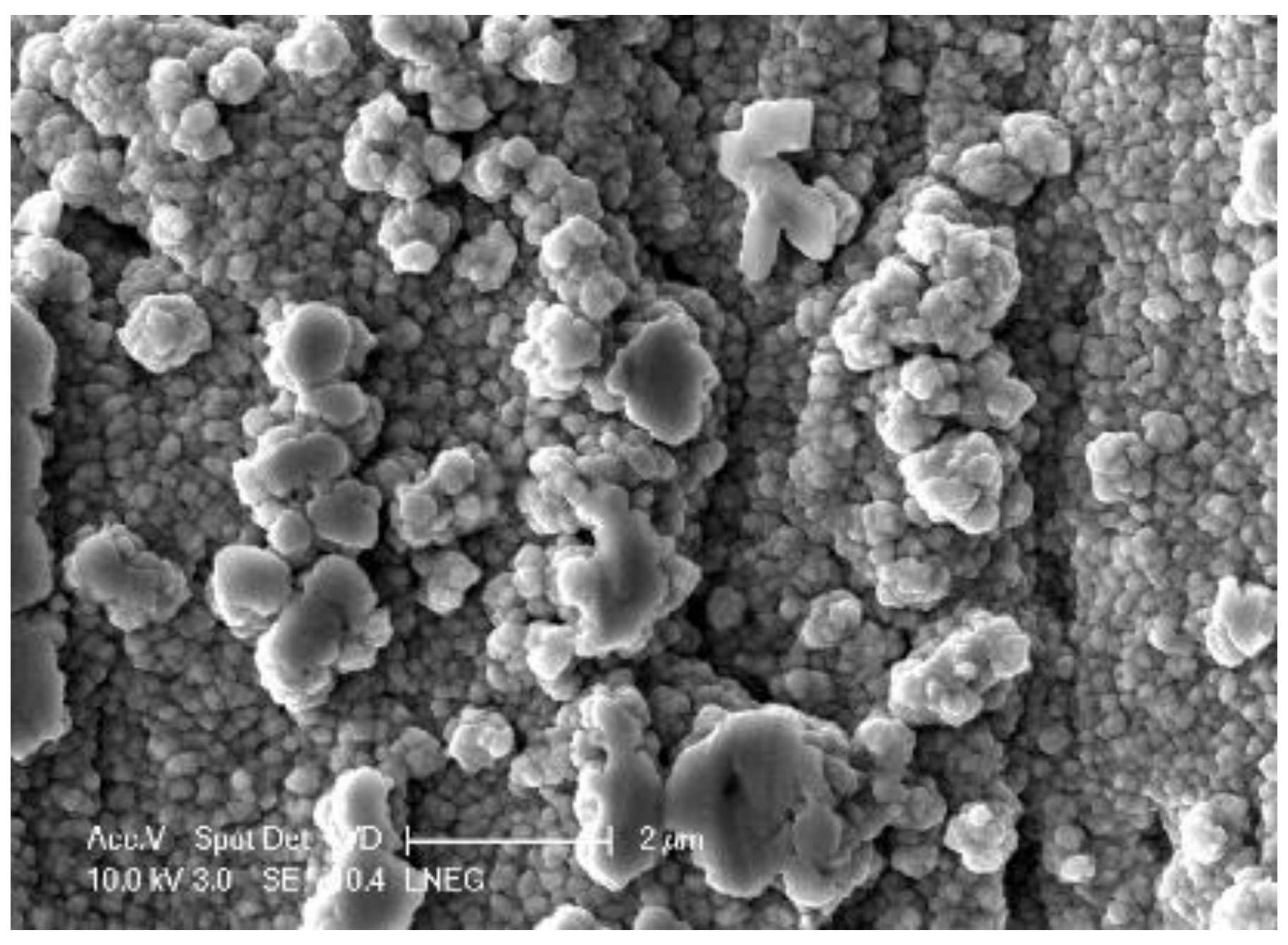


Fig. 7 – SEM-SE image of a patinated silver sample (Ag4) showing a compact, homogeneous patina with well-defined boundary particles. A second patina, consisting of loosely dispersed particles, appears to be forming above it.

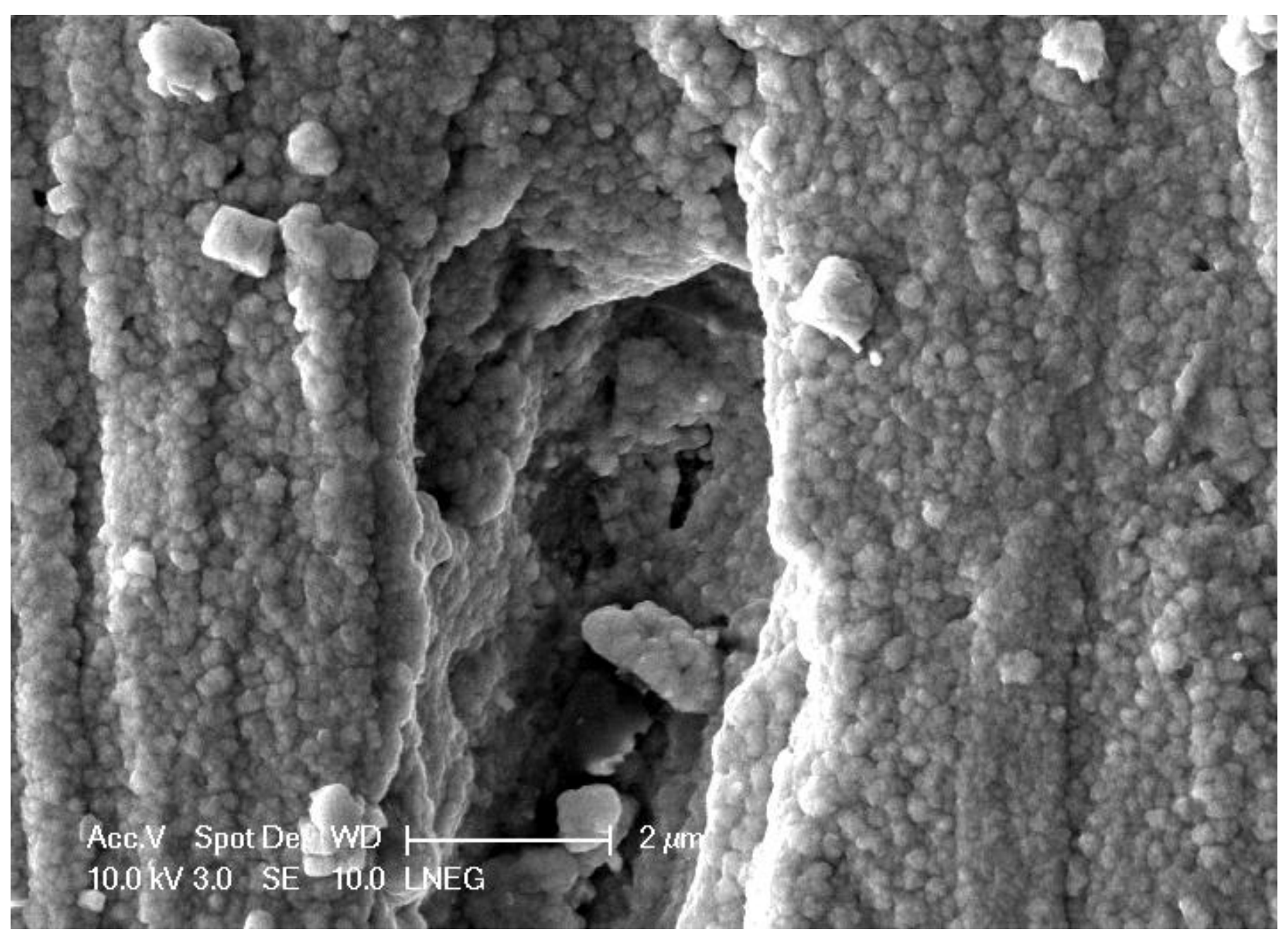


Fig. 8 – SEM-SE image of a patinated silver sample (Ag5) after corrosion illustrating the onset of corrosion, with particles losing definition and the surface becoming irregular. The initially uniform patina structure begins to dissolve upon corrosion, exposing a more disrupted morphology.

CONCLUSION

Colorimetry offers an effective, non-invasive methodology for distinguishing original patinated silver surfaces from those altered by natural corrosion, as supported by SEM imaging of surface degradation. These findings highlight its value in conservation and restoration practices. Real-time monitoring of color changes during cleaning enables informed decision-making and helps preserve the original decorative finish.

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