Electrochem Origalys Application Note

APPLICATION NOTE

Cleaning of silver objects by electrochemical methods

This application example, carried out in collaboration with the Arc'Antique laboratory, demonstrates how electrochemistry can be used for cleaning tarnished silver objects.

General Electrochemistry AP-GE20

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Summary:

Electropolishing cleaning

The cleaning of silver objects requires methods that are precise, non-destructive, and non-abrasive. Among the common techniques, cathodic polarization represents a suitable approach for controlled cleaning and restoration of tarnished metallic surfaces, without the use of mechanical abrasion or aggressive chemical agents.

In this application example, the treatment involves two steps:

- A first step of Cyclic Voltammetry (CV) to identify the reduction peak potential of the studied sample,
- A second step of Chronoamperometry (CA) to apply this potential. This not only restores the metal's shine but also preserves the material in its entirety.

However, applying this method to heritage objects requires fine control of the electrochemical parameters, particularly the applied potential and exposure time. Polarization at an excessively high potential can lead to hydrogen bubbling, which may irreversibly damage the object. It is therefore recommended to always consult a heritage professional for its implementation.

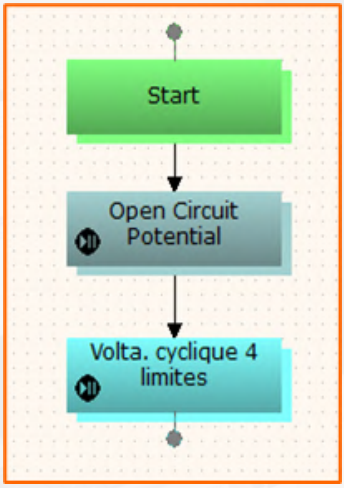
The first essential step is to characterize the electrochemical behavior of the object before any treatment. Four-limit Cyclic Voltammetry (CV 4-limits) makes it possible to determine the potential ranges of oxidation and reduction, identify active electrode reactions, and anticipate critical thresholds beyond which the metallic surface may suffer undesirable degradation. This constitutes a crucial preliminary step in defining an optimized Chronoamperometry (CA) treatment, ensuring effective cleaning without material loss. Figure 2 shows the test object: a silver spoon.

Figure 2: Reneka 24 silver-plated metal spoon studied

Cyclic Voltammetry Parameters

The experiments were carried out using the OrigaMaster 5 software. Figure 3 shows the flowchart of the CV and presents its parameters.

Figure 3: Flowchart and parameters of the 4-limits CV



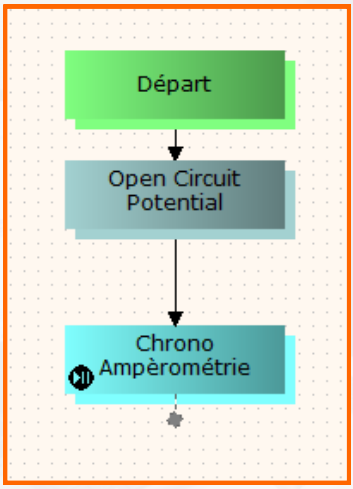
Pot. CV 4 limits	
Initial (mV)	0, FREE
Vertex 1 (mV)	0, FREE
Vertex 2 (mV)	-2500, FREE
Value	-2500
versus	FREE
Final (mV)	-2500, FREE
Value	-2500
versus	FREE
Scan rate (mV/sec.)	10, 0.06, 0.6
Sampling rate 1 point o...	1
Cycle	0
Maximum current (mA)	10
Minimum current (mA)	-10
Ohmic Drop Comp.	No
Maximum range	Auto
Minimum range	Auto
Digital Filter	0
Auxiliary input	Vs
Open circuit at end	Yes
Rejection 50 Hz	Yes

Note: Before the potential sweep, an OCP (Open Circuit Potential – free potential measurement) is performed to allow the system to reach equilibrium with the solution.

CA Parameters

Figure 4 shows the CA flowchart and outlines its parameters.

Figure 4: CA flowchart and parameters



Chrono Amperometry	
Potential 1 (mV)	-200, FREE
Duration 1	2, min.
Potential 2 (mV)	-1182, REF
Duration 2	11, min.
Meas. period (sec.)	0.1
Cycle	1
Ohmic Drop Comp.	No
Maximum range	Auto
Minimum range	Auto
Maximum current (...	500
Minimum current (m...	-500
Open circuit at end	Yes
Auxiliary input	No
Rejection 50 Hz	Yes

NOTE: The potential selected for the CA corresponds to the maximum of the peak determined during the previous CV measurement (make sure to express the value with respect to the reference electrode (REF)). Correction: After the CV, the potential is determined relative to the reference electrode. Be careful not to indicate a specific potential value, as it depends on the reference electrode and may mislead the reader.

Results and Discussion

CV results :

Figure 5 shows the voltammogram obtained with the 4-limits CV. Using the 'Min Max' tool in the 'Math' menu (Figure 6), the optimal potential to be applied is found: –1182 mV/SCE.

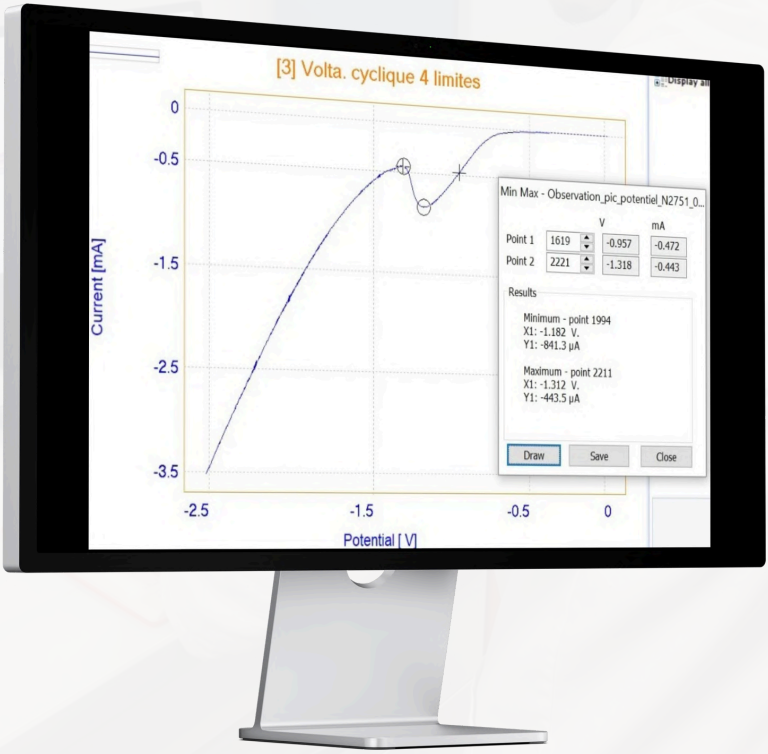


Figure 5: The reduction potential of -1182 mV is extracted from the voltammogram for the next step

Results and Discussion

CA results :

Figure 6 shows the resulting curve.

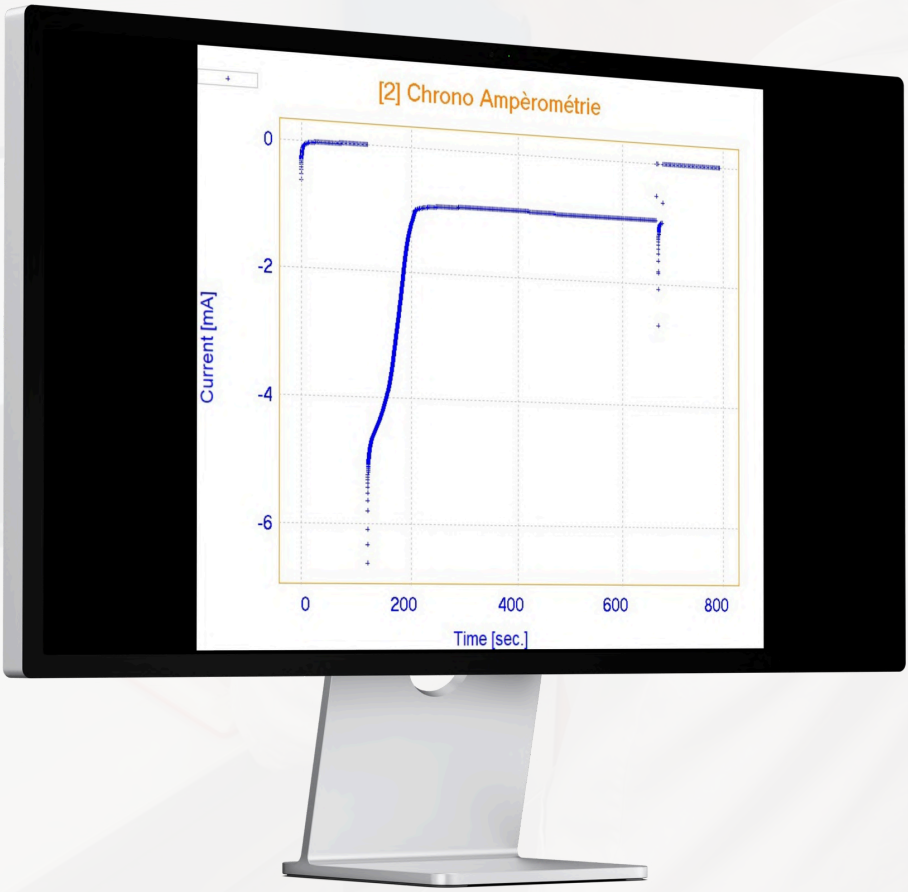


Figure 6: Chronoamperogram

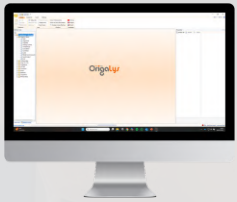
Conclusion

After 11 minutes of polarization, the immersed part of the spoon regained its shine, as the corrosion product responsible for tarnish (mainly silver sulfide) was reduced back to silver. The treatment duration depends on the amount of silver sulfide to be reduced.

Figure 7: Spoon after restoration by electropolishing

Necessary instruments and materials

OGF+01A



OrigaMaster 5

REF: ECS Electrode

AUX: Platinum Electrode

WRK: Silver-plated metal spoon
Reneka 24

- Electrolyte: 0.01 M sodium sulfate solution

Presentation of the laboratory

Conservation-restoration involves intervening on cultural heritage objects to ensure their preservation, conservation, study, and to facilitate their interpretation, while respecting their integrity. In France, the Heritage Code regulates the conservation-restoration of museum and archaeological works.

The Arc'Antique laboratory, specialized in the conservation-restoration of terrestrial and underwater archaeological heritage, brings together a team of more than 14 experts in imaging, analysis, research, and conservation-restoration, recognized by the French State.

Arc'Antique is a department of Loire-Atlantique. It thus forms part of the wider archaeological framework—from excavation to museum display—within the Grand Patrimoine sub-directorate of Loire-Atlantique.

The main missions of the Arc'Antique laboratory are:

- The study and conservation-restoration of terrestrial and underwater archaeological objects
- The development of applied research programs
- Dissemination and sharing of knowledge with schools, students, and professionals.

Figure 1: Restoration of a work [1]
Photo: L. Preud'homme Grand Patrimoine Loire-Atlantique

[1]: 2023107-102 Torch, 1740, Inventory number 896.1.4011
Under the base: Master mark of Jacques Pimot, silversmith.
On the base: Coat of arms of the Kervégan family (Kervégan (de) Christophe-Clair Danyel) and 4 hallmarks

Have an idea for an Application Note ?

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