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LOCAL CLEANING WITH THE PLECO ELECTROLYTIC PENCIL OF THE TARNISHED SAINT CANDIDE RELIQUARY HEAD AT THE TREASURY OF SAINT-MAURICE ABBEY, VALAIS (SWITZERLAND)

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Abstract

The *Pleco*, a new electrolytic pencil, was used for the local cleaning of silver plates nailed to the wooden core of the reliquary head of Saint Candide, one of the masterpieces in the Treasury of Saint-Maurice Abbey, Valais (Switzerland). The versatility of the tool is demonstrated in terms of its ability to precisely determine the type and amount of tarnish on a series of plates, to define the parameters to electrolytically clean the metal surface and to safely carry out the cleaning treatment for this composite artefact. The local and specific cleaning of each plate ensures the surface rendering of differing plates does not appear overly uniform.

1 Introduction

A new electrolytic pencil was designed by the Conservation Research Unit at the University of Applied Sciences and Arts of Western Switzerland Arc (UR-Arc CR). It was developed during research which aimed to locally clean silver tarnish on composite artefacts in the Treasury of Saint-Maurice Abbey, Valais (Switzerland).¹ The research was conducted to prepare for the 1500th anniversary of the Abbey and an exhibition of the restored works in a new hall.²

Named the *Pleco*, after the fish which cleans aquariums (http://fr.wikipedia.org/wiki/Hypostomus_plecostomus), this pencil enabled cleaning of tarnished silver plates nailed to the wooden cores of many reliquaries. The tip of the pencil features an electrolytic cell enclosed by a micro-porous foam pad which is impregnated with an electrolyte. The electrolyte is constantly renewed by membrane pumps. The cleaning process is based on the electrolytic reduction of tarnish compounds.¹

The treatment of the different plates is customised to their specific condition. These plates and corresponding artefacts are from different periods and have different compositions. The oldest artefact dates from the 6th century, while the newest one is from the 20th century. Some artefacts have already been restored and plates might have been replaced. As a result, the silver tarnish over the whole surface of each artefact is not necessarily homogenous. To achieve a cleaning that adapts to the type and the amount of tarnish, the treatment parameters must first be determined for each of the plates.

The cleaning of silver tarnish on the composite artefacts of the Treasury of Saint-Maurice Abbey is just one of the steps in their conservation treatment. Its set-up and implementation comprise a strategy that is presented in this paper for the reliquary head of Saint Candide.

2 Materials and methods

2.1 The reliquary head of Saint Candide

This prestigious artefact was made in 1165 by a silver-smith in Saint-Maurice. It is a life-size bust representing Candide, senator of Theban soldiers, one of the Christian martyrs of Agaune (Figure 1a). The front plate of the base depicts the martyrdom scene with the inscription "While Candide is sacrificed with the sword, his spirit ascends to heaven; in exchange of his death, life is given to him", Figure 1b).³ The reliquary head comprises silver plates partly gilded with black patterns suspected to be niello, which are nailed on a wooden core (walnut). They are decorated with filigree, precious stones and rock crystals. Also there are copper plates with enamel: *champlevé*. The reliquary was opened on two occasions; in 1659 (for identification of the relics) and in 1800 when the wooden core was abruptly broken to access the relics. In 1961, the silver plates were dismantled during the restoration of the reliquary head.⁴

Since significant differences in the composition of the plates might influence the tarnish and as a result their electrochemical and electrolytic responses during the treatment,⁵ they were analysed, after being degreased, with a portable X-ray fluorescence spectrometer (NITON XL3t 950 Air GOLDD+ analyser, Thermo Fischer®, Table 1).

These analyses which were carried out on 17 representative plates of the reliquary head show that their copper concentrations are low: around 1.2 to 1.8% by weight. They contain small amounts of gold (around 0.4-0.5% by weight) and lead. These results are similar to those found on other medieval artefacts.⁶ The plate on the face and one on the feet have the highest copper concentration, while the front plate of the base



Figure 1: a) The reliquary head of Saint Candide in its showcase (old treasury). b) A detail of the front plate on the base and its inscription (© Atelier de l'Abbaye de Saint-Maurice).

		Ag	Cu	Au	Pb	Sn	Fe
		% in weight					
Hair	Back proper left	97.9±0.2	1.49±0.04	0.49±0.02	<	-	<
	Back proper right	98.0±0.2	1.43±0.04	0.47±0.02	<	-	<
	Front proper left	98.0±0.2	1.42±0.04	0.48±0.02	<	-	<
	Front proper right	97.9±0.2	1.45±0.04	0.51±0.02	<	-	<
Face	Proper left side	97.8±0.2	1.85±0.04	0.36±0.02	<	-	<
Neck	Back	97.9±0.2	1.46±0.04	0.47±0.02	0.10±0.01	-	<
	Back proper left	98.2±0.2	1.40±0.04	0.37±0.02	<	-	<
	Back proper right	98.2±0.2	1.31±0.04	0.36±0.02	<	-	<
Shoulders	Proper left	98.2±0.2	1.29±0.04	0.37±0.02	0.12±0.01	-	<
	Back	97.9±0.2	1.50±0.04	0.48±0.02	<	-	<
	Proper right	98.2±0.2	1.30±0.04	0.36±0.02	0.11±0.01	-	<
Base platform	Back proper left	96.6±0.2	1.40±0.04	0.50±0.02	0.13±0.01	-	0.90±0.05
	Back	97.6±0.2	1.31±0.04	0.53±0.02	0.10±0.01	-	0.45±0.04
	Back proper right	97.9±0.2	1.21±0.04	0.49±0.02	<	-	0.26±0.04
	Restoration - Back proper right	97.0±0.2	1.69±0.04	0.51±0.02	<	0.15±0.07	0.53±0.05
	Front	97.6±0.2	1.48±0.04	0.48±0.02	0.11±0.01	-	0.25±0.04
Front plate of the base		98.3±0.2	1.17±0.04	0.37±0.02	0.12±0.01	-	<

Table 1: X-ray fluorescence analyses (with errors) on 17 of the 33 silver based plates of the reliquary head of Saint Candide. Elements that are below the limit of detection are indicated with symbol <, while unidentified elements are indicated with symbol -.

and another plate of the feet have the lowest copper concentration. Furthermore the plates of the platform of the base and some plates in the base additionally contain small amounts of iron.

As described below, the entire surfaces of the silver plates are tarnished. An electrolytic cleaning process is preferred since it cleans the silver tarnish without being invasive – unlike traditional cleaning methods based on chemical and mechanical processes. The treatment in 2000 by immersion of the dismantled plates in the shrine of Saint Sigismund and his children could not be used here.⁵ The permitted treatment time was too short. Also, the dismantling of the plates of the reliquary head in 1961 had revealed historical and technical information that did not require further investigation. Therefore the need arose for a tool which could locally and electrolytically clean the tarnished metal plates.

2.2 The Pleco

The electrolytic pencil, called the Pleco, is the result of a multidisciplinary research project carried out by the members of the UR-Arc CR, the Laboratoire de recherche en anthropotechnologie (EDANA) at HE-Arc Engineering, Neuchâtel, in collaboration with the conservation workshop at the Abbey and the Neuchâtel FabLab (small-scale digital fabrication workshop).¹ The Pleco is a tool built from a kit. The drawings of the parts comprising the Pleco are open-source documents that can be downloaded from www.fablab-neuch.ch/pleco. The components are made by 3D printing and laser cutting; two techniques that are usually available in the FabLabs which operate in several countries.

The Pleco is composed of four sets of parts. The *pencil core* contains the electrodes: a vitreous carbon rod as the reference electrode (Metrohm® 0.3 V/SHE - Standard Hydrogen Electrode) and a platinum rod as

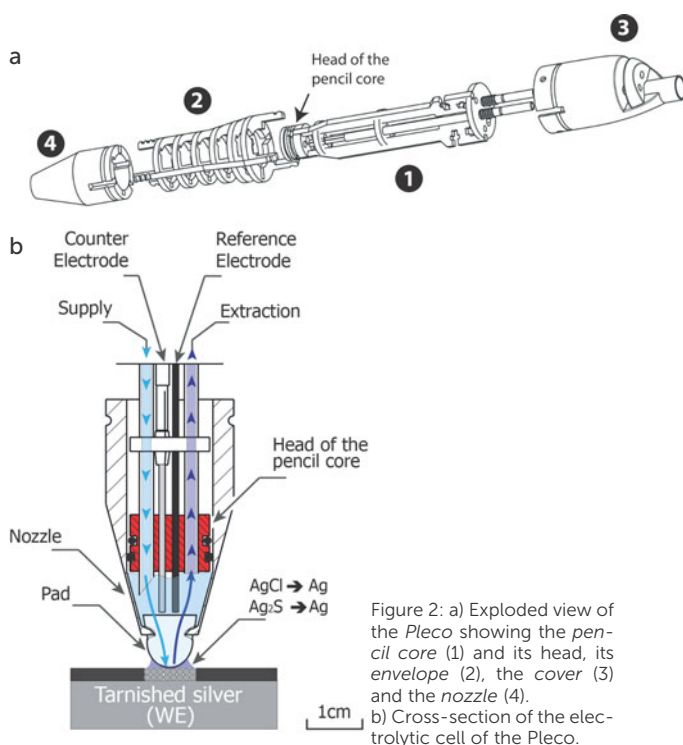


Figure 2: a) Exploded view of the Pleco showing the pencil core (1) and its head, its envelope (2), the cover (3) and the nozzle (4). b) Cross-section of the electrolytic cell of the Pleco.

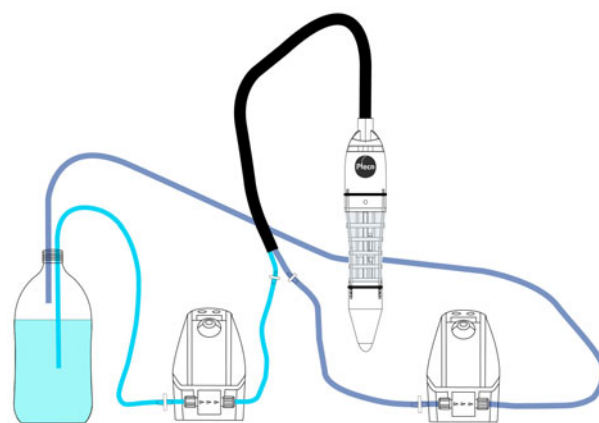


Figure 3: Schematic of the first prototype of the electrolytic pencil, the reservoir and two diaphragm pumps for circulating the electrolyte.

the counter-electrode. The electrodes are secured inside a mandrel, while a pair of tubes supply and extract the electrolyte. An *envelope* houses the pencil core, while the *cover* features a push-button for operating the electrode mandrels. Lastly, the *nozzle* contains the electrolytic cell (Figure 2a). The volume of the cell is determined by the head of the pencil core and the nozzle (the volume of the cell is variable: 1.5–3 mL). Its watertightness is ensured by O-rings. Teeth in the tip of the nozzle retain the micro-porous polyvinyl formal (PVFM) foam pad which is put in contact with the tarnished silver – the working electrode (Figure 2b).

The electrolyte is sodium nitrate buffered with sodium citrate / citric acid – NaNO_3 1% by weight (slightly acidic – pH = 5.4). The supply and extraction of electrolyte is made using two membrane pumps (SIMDOS 10, KNF®). They control flow and prevent leakage of the electrolyte from the pad which contacts the surface of the metal being cleaned (Figure 3). The pumps function in a closed circuit and are set so the apparent flow for extraction is slightly higher: + 10 mL/min. To dilute the extracted polluting species, the volume ratio of the electrolytic cell to the reservoir is 1: 1000.

The correct wetting of the PVFM foam pad with the circulating electrolyte is first checked on a flat silver coupon that simulates the surface of the object being cleaned.

2.3 Devices and electrolytic plots

Determining the treatment parameters is carried out using linear voltammetry in the cathodic field while the Pleco is used in *static mode*: securely positioned on against a tarnished surface (Figure 4a). Electrical contact is made using an aluminium strip attached to the object with adhesive tape (red arrow). The area (1 cm^2) investigated is degreased with ethanol before linear voltammetry. Using a potentiostat (Origalys®, Origastat e200), the potential of the material is scanned from E_{corr} (i.e. without applied current) to a negative potential as low as $-2 \text{ V/vitreous carbon reference electrode (VC)}$. The scanning rate is 10 mV/s . Because of the production of noxious hydrogen sulphide, H_2S , it is also recommended to work in a fume cabinet or with a local extraction trunk. An example of a linear voltammetric plot obtained from the head of Saint Candide shows two reduction peaks: I ($\text{AgCl} \rightarrow \text{Ag}$) and II ($\text{Ag}_2\text{S} \rightarrow \text{Ag}$) (Figure 4b, black curve). AgCl is pro-

Before any intervention, the reliquary head was documented in detail to determine the conservation state of each plate. Some are fragile, even fragmentary, and the movement of the Pleco over them needed to be carefully performed. This thorough examination was the opportunity to determine which borders should be protected with an adhesive tape before the treatment to prevent any risk of leakage (Figure 10a) and to complete the surface degreasing of the plates.

3.1 Type and amount of tarnish of the plates of the reliquary head

Similar cathodic voltammetric plots to those in Figure 4b were acquired from each plate on the reliquary head. Both AgCl and Ag₂S tarnish were observed but with different amounts; as indicated in Figure 7 where the potentials of the maxima of the reduction peaks for the more tarnished plates are shifted towards more negative values.

Equivalent plots were systematically produced from the entire series of plates. The results acquired enabled the observation that AgCl tarnish (outlined in orange in Figure 8) is prominent (plots B and C in Figure 7) on the base of the reliquary head (solid lines) and more so where the artefact is handled (orange arrows in Figure 8) or where significant reliefs are present (such as on the front plate of the base). Since there is less AgCl tarnish on the upper part of the reliquary head and on its back, it seems as though these parts have been handled less (plot A on Figure 7 and dotted lines 8).

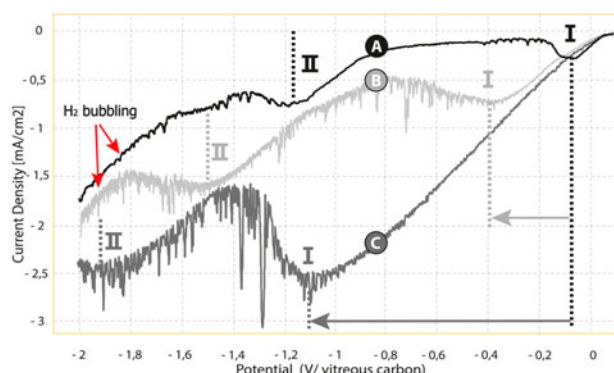


Figure 7: Cathodic voltammetric plots for three plates of the reliquary head enabled determination of the different types and amounts of tarnish. Peaks I (AgCl→Ag) and II (Ag₂S→Ag) started at the same potential (versus vitreous carbon) irrespective of the amount of tarnish. But their maximum was shifted negatively according to the amount of tarnish (grey lines with arrows for peak I). Plate A is slightly tarnished, plate B is moderately tarnished and plate C is highly tarnished.



Figure 8: Mapping of the tarnish on the reliquary head using cathodic voltammetric plots. The tarnish due to AgCl and Ag₂S are respectively underlined in orange and black: major (solid lines) and minor (dashed lines) (© Atelier de l'Abbaye de Saint-Maurice).

The Ag₂S tarnish (outlined in black in Figure 8) covers the whole surface of the reliquary head, but it is less prominent on its back, which was adjacent to the rear wall of the showcase.

The voltammetric plots showed clearly that the tarnish was influenced by the handling of the reliquary head and the presence of sulphur species while the difference in composition of the plates had a minor role.

3.2 The treatment parameters

As shown on Figure 7, the different types of tarnish should theoretically all be reduced at -1.8 V/VC. However, if this potential were to have been applied on the entire series of plates, unwanted effects would have arisen:

- evolution of hydrogen bubbles that would have weakened the plates that are slightly and moderately tarnished (plots A and B in Figure 7),
- over-cleaning (due to the bubbling of hydrogen) of metallic surfaces would have occurred and increased the non-aesthetic contrast between well preserved and cleaned plates, plates with losses and other materials that conserve traces of use,
- damage to the vitreous carbon reference electrode which is weakened at these potentials.

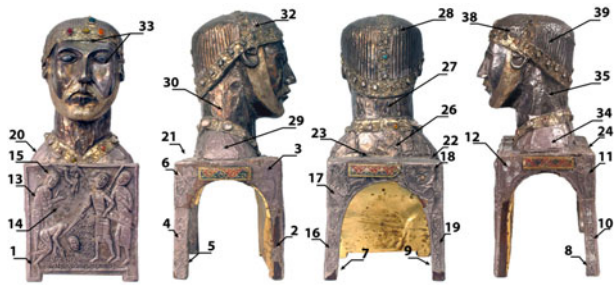
The cleaning of the artefacts of the Treasury of Saint-Maurice Abbey must be gradual and should enable visual appreciation of their historic nature. As a result, we preferred to clean the tarnish of all plates in several steps, starting with the AgCl tarnish and continuing with the Ag₂S tarnish. According to the plots in Figure 7, the potentials applied were:

- -0.9 V/VC for reducing AgCl on slightly and moderately tarnished plates (plots A and B),
- -1.5 V/VC for reducing AgCl on highly tarnished plates (plot C) and Ag₂S on slightly and moderately tarnished plates (plots A and B),
- -1.8 V/VC for reducing Ag₂S on moderately and highly tarnished plates (plots B and C).

These three potentials are not systematically those of the maxima of the reduction peaks. Instead they correspond with average values for which reduction should be effective.

Using this approach the reduction potentials were established from each plate. The treatment times were determined by chrono-amperometry, as indicated on Figure 5b. Table 2 presents the results obtained on the plates of the 4 sides of the reliquary head. The potentials applied and the cumulated treatment times (AgCl + Ag₂S) reflect the level of tarnish on the different plates. The reduction durations range from 50 s for the slightly tarnished plates to 100 s for the moderately to highly tarnished plates.

The whole series of linear voltammetric and chrono-amperometric plots were completed in two days during which neither the electrolyte nor the pad were changed. Instead the pad was regularly rinsed of its local stains. The rinsing process is described in the discussion section.



Side of the object	plates / measurement points	-0.9 V/VC AgCl→Ag (s)		-1.5 V/VC AgCl/Ag ₂ S→Ag (s)		-1.8 V/VC Ag ₂ S→Ag (s)	
		Duration (s)	Tarnish Level	Duration (s)	Tarnish Level	Duration (s)	Tarnish Level
Face	1	15-20	M			20	M
	13	30-45	M			25-30	M
	14	15-20	S	20	S		
	15			20-50	H	30-50	H
	20	20	M	50-75	M		
	33	10	S	15	S		
Proper right	2			40	H	?	H
	3			100	H	?	H
	4	50	M	20	M		
	5	20	M			25	M
	6	50	M			20	M
	21			40	H	?	H
	29	20	M	30	M		
	30	10	S	20	S		
Back	7	40	M			30	M
	9			25	H	50	H
	16	20	S	30	S		
	17	15	S	30	S		
	18	15	S	20	S		
	19	15-30	S	40	S		
	22	40	M	50-75	M		
	23	20	M	?	M		
	26	15	M	30-40	M		
	27	10-15	M			30-40	M
Proper left	8	40	M			30	M
	10	50	M	25	M		
	11	50	M			40-50	M
	12			120	H	25	H
	24	20	M			40	M
	34	30	M	20	M		
	35	10	S	25	S		
	38	15-20	S	20	S		
	39	20	S	50	S		

Table 2: Electrolytic cleaning durations according to the potentials applied on each plate of the four sides of the reliquary head: (© Atelier de l'Abbaye de Saint-Maurice).

S - slightly tarnished plates
M - moderately tarnished plates
H - highly tarnished plates



Figure 9: Saint Candide reliquary head before (a), during (-1.5V/VC) (b) and after the polishing treatment (c), © Atelier de l'Abbaye de Saint-Maurice.

3.3 Treatment of the reliquary head in dynamic mode

After the treatment parameters had been determined for all the plates, the treatment was setup. The shape of the artefact is complex and its movement in a fume cabinet was hindered. To limit handling of the reliquary head, the plates on one side were treated at the respective potential before repeating the protocol on the other sides. The treatment started at -0.9 V/VC on the slightly and moderately tarnished plates where only AgCl was reduced. Apart from plates 2, 3, 9, 12 and 21 and the reliefs on the front plate of the base (area 15), the plates were treated for the durations given in Table 2 and rinsed afterwards in deionized water with cotton swabs. At the end of this step the metal surface of the reliquary was visually inspected as a whole. The first reduction treatment yielded a noticeable aesthetic improvement in the appearance of the metal surface. Since the original appearance of the object was probably more lustrous, we applied the procedure at -1.5 V/VC and for durations determined from the series of plates indicated in Table 2. This second step entailed reducing Ag₂S tarnish on the plates which had previously had their AgCl tarnish reduced. The treatment at -1.5 V/VC was also used to reduce the AgCl on the highly tarnished plates or areas (2, 3, 9, 12, 15, 21). The plates cleaned were once again rinsed. The surface appearance of the reliquary became more lustrous (Figure 9b, note that the object is photographed from a different angle), with the exception of reliefs of some plates that required reduction at -1.8 V/VC. Once again the treatment conditions are given in Table 2.

At the end of these electrolytic polarisations, the surfaces of the series of metallic plates were re-rinsed in deionized water applied with cotton swabs. The appearance of the metal remained too matte, so the reduced silver was slightly burnished with unbleached cotton cloth (Selvyt SR®). This step produces a more lustrous appearance and the conservator decides on the level of this final cleaning to maintain observable relief to the overall visual impression of the piece (Figure 9c).

Some areas of the head (edges of the plates, filigree, niello, stones, crystals, gilding) required complementary means of cleaning with soft brushes wet with a water-alcohol solution (1:1).

The reliquary head like objects of the Treasury of Saint-Maurice Abbey that have been restored are now exhibited without any surface protection in showcases with internal drawers containing Silicagel®.

4 Discussion

Although the risk of leaking electrolyte is limited by the design of the Pleco, extra precautions were taken to further reduce this risk. The shape of the pad (flat, round, sharp) was adapted according to the surface. Also, adhesive tape was applied where plates overlapped and more particularly on areas where plates produced a sharp angle between them (Figure 10a). Access to these areas was difficult with the Pleco; so extra force was required to deform the pad into shape. In some cases this caused leakage of several drops of electrolyte which were swabbed away before starting the cleaning process.

Where prominent reliefs or metal burrs could dislodge the pad from the nozzle, the movement of the Pleco was performed incrementally rather than continuously over the treated surfaces (Figure 10b), making sure that all tarnished areas were cleaned.

To remove residues from the reduction processes, the metal surface was regularly cleaned with a cotton swab and rinsed. During the chrono-amperometry step, and more particularly on heavily tarnished plates, the tip of the pad became darkened with pollutants. This pollution was removed by repeatedly pressing the pad while the electrolyte was still circulating (Figure 11). If the black staining persisted, the pad was replaced while the pumps were switched off. After replacement of the pad, the pumps were switched back on the circulation and any leakage was rechecked.

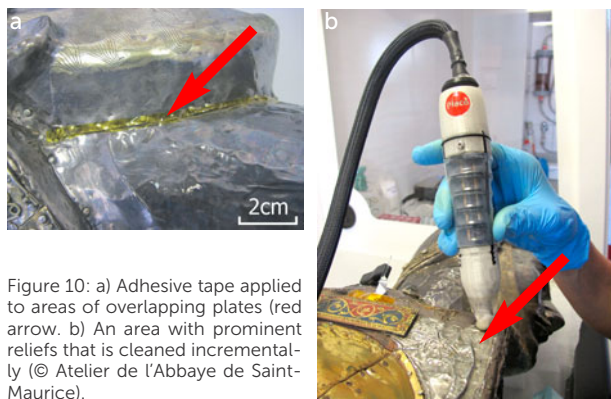


Figure 10: a) Adhesive tape applied to areas of overlapping plates (red arrow). b) An area with prominent reliefs that is cleaned incrementally (© Atelier de l'Abbaye de Saint-Maurice).

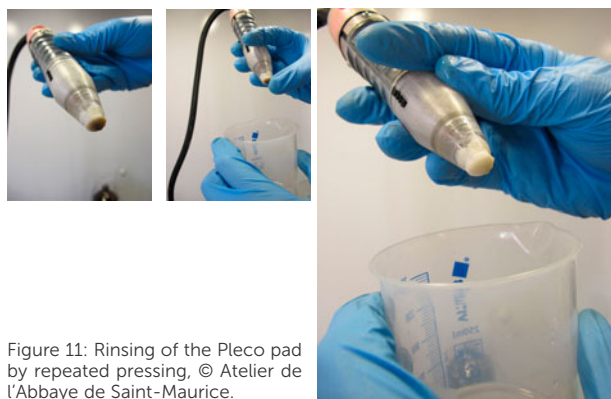


Figure 11: Rinsing of the Pleco pad by repeated pressing, © Atelier de l'Abbaye de Saint-Maurice.

With time the electrolyte in the reservoir yellowed due to the pollution with sulphur species (strong evolution of H_2S was observed). The electrolyte was changed for a new solution to prevent any re-staining of the metal surface, particularly when it was not polarised (at the moment when the Pleco was put in position). A further development of the system would be to trap these sulphur species to make sure that the electrolyte remains clean during the whole cleaning process.

The local electrolytic cleaning might appear a time-consuming process for artefacts with complex shapes and with different amounts of tarnish: 2 days for the determination of the parameters followed by 2 weeks of treatment on the reliquary head. Furthermore it required the contribution of corrosion scientists who are able to interpret voltammetric and chrono-amperometric plots. Still the investment was worth it since the treatment was performed afterwards in safe conditions and the required time was much less than the time needed to dismantle the plates: several months.

5 Conclusion

On the whole, using the Pleco to locally clean the silver tarnish on the metallic plates of the Saint Candide reliquary head was satisfactory. The electrolytic pencil is a versatile tool, for evaluating the type and amount of tarnish and defining the electrolytic cleaning parameters, and for actually performing a safe and local cleaning: without dismantling this composite artefact.

By avoiding the dismantling the cleaning protocol respected its integrity. The Pleco enabled the conservator to choose the level of cleaning. The treatment is adaptable, and refining the appearance is possible.

Since we have validated the Pleco for restoration practice, we will now pursue its application on other composite artefacts at the Treasury of Saint-Maurice Abbey, particularly the partly gilded ones. This will permit optimisation of the Pleco and specification of its limits of use. Other applications are planned; including the cleaning of silver foils on leather panels, and the stabilization of actively corroding lead artefacts which are still attached to organic components, e.g. lead seals (*bullae*) attached to parchment or cloth. The eventual experiences from these different applications will be added to the webpage forum for the Pleco: www.fab-neuch.ch/pleco. They should generate open discussions and help optimise the local electrolytic treatments for interventive conservation and restoration of cultural heritage.

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