A new electrolytic pencil for the local cleaning of silver tarnish

Christian Degrigny1, Romain Jeanneret1, Denise Witschard2, Carole Baudin3, Gaëtan Bussy4, Hélène Carrel5

1HE-Arc CR, Haute Ecole Arc Conservation-restauration, Neuchâtel, Switzerland, 2Atelier de conservation-restauration, Abbaye de Saint-Maurice, Switzerland, 3Laboratoire de Recherches en Anthropotechnologie – EDANA, Haute Ecole Arc Ingénierie, Neuchâtel, Switzerland, 4FabLab, Neuchâtel, Switzerland, 5Hélène Carrel Workshop, Switzerland

The prototyping of a newly designed electrolytic pencil for the local cleaning of silver tarnish on artifacts comprising inseparable organic components is described. The pencil helps determine the type and amount of tarnish, define the cleaning parameters (treatment potential and duration), and provides a safe and efficient way to locally and electrolytically reduce silver tarnish. The electrolyte is conveyed to and from the surface of metal objects via a micro-porous foam and is continuously renewed by two pumps. This user-friendly and ergonomic pencil is distributed as an open source kit for self-assembly with parts fabricated using innovative and low-cost technologies. The operating modes for the pencil are described. To evaluate this new tool, the pencil was used to clean a selection of tarnished silver components from composite masterpieces in the Treasury of Saint-Maurice Abbey.

Keywords: Silver artifacts, Silver tarnish, Composite, Cleaning, Electrolytic pencil, 3D printing, Laser cutting, Open source

Introduction

Many silver artifacts are composite. They are not only made of silver, gilded silver, or even gilded copper sheet, but also contain wooden elements as their cores (e.g. reliquaries and shrines) (Fig. 1). They can also be decorated with colored glass, precious stones, enamels, pearls, and niello – the dark decorative surface finish comprised of metallic sulfides (Oddy et al., 1983).

Often these objects have been extensively altered over time. The most apparent deterioration is the tarnishing of the silver which blackens its original metallic luster (Costa, 2001). For silvered brass and silver–copper alloys, copper tarnish can result; copper oxides and sulfides (Degrigny et al., 1993). Cleaning silver tarnish from composite artifacts presents many problems for conservator-restorers. If dismantling is not possible, cleaning methods are restricted to the use of abrasive compounds. Today this type of intervention is considered too drastic as loss of underlying metal occurs with each cleaning, in addition to the silver compounds comprising the tarnish above. Furthermore, abrasive cleaning can leave residues on the metal surface, which are visually distracting and might cause local instability (Costa et al., 2006). As a result, conservators might advocate the temporary dismantling of artifacts to separately treat the metallic parts by immersion in chemical or electrolytic baths (Degrigny & Witschard, 2006).

Electrolytic cleaning is a controllable process applied to historic objects which involves very little material loss. When the metal is cathodically polarized, the chemical species which comprise the tarnish (e.g. silver chloride, AgCl, produced by handling artifacts and/or silver sulfide, Ag2S, due to atmospheric sulfur species) are reduced to elemental silver, Ag (Degrigny, 2010). The cathodic potential applied depends on the type of tarnish (AgCl or Ag2S) and its amount. Indeed, cleaning of thicker tarnish requires more negative cathodic potentials (Degrigny & Witschard, 2006; Witschard et al., 2015). A light burnishing of the surface restores the metallic luster. The treatment is carried out by immersion, either in sodium sesquicarbonate (or trisodium hydrogencarbonate – Na3H(CO3)2) 5% by weight (alkaline) (Degrigny et al., 1993, Degrigny & Jérôme, 1993), or in sodium nitrate buffered with citrate – NaNO3 1% by weight (slightly acidic) (Degrigny et al., 1996). In the alkaline electrolyte, an anode of stainless steel grid is used while a more expensive but corrosion resistant platinum (Pt) mesh is necessarily employed for neutral
These polarizations are quite fast (a few minutes) and are performed in chrono-amperometric mode (i.e. monitoring of the reduction current while applying a constant potential). For heavy tarnish, several cathodic polarizations are necessary and require replacement of the polluted electrolyte. Because of the production of noxious hydrogen sulfide, H$_2$S, it is also recommended to work in a fume cabinet or with a local extraction trunk. If the silver is gilded, the tarnish reduction step is followed by a controlled oxidation to dissolve any superficial deposits of reduced silver. The gilded silver plates comprising the shrine of Saint Sigismond and his children at the Treasury of Saint-Maurice Abbey were cleaned using this process after they were dismantled from their wooden core (Degrigny & Witschard, 2006).

Often the systematic dismantling of artifacts with tarnished silver parts is neither possible (due to a lack of time) nor desirable (harmful to the object). So when the Saint-Maurice Abbey decided in 2011 to have the masterpieces in their Treasury restored for its 2015 Jubilee, their commission wanted to explore approaches to cleaning which did not involve dismantling (Witschard et al., 2015).

The first publication about an electrolytic pencil for conservation-restoration was in 1986. Aldaz et al. suggested using a plastic cylinder containing an electrolyte and an anode and featuring a porous tip to stabilize actively corroding metal surfaces. A drop of electrolyte was manually inserted between the tip and the object under treatment (the cathode). This pencil did not provide control of the cathodic potential, nor renewal of the electrolyte. Twenty-five years later, controlled and local electrolytic reductions of heritage metals were tested simultaneously at the J. Paul Getty Museum (Los Angeles, USA) to clean gilded silver objects (Wolfe et al., 2010) and at Arc’Antique (Nantes, France) to stabilize active corrosion on lead- and copper-based artifacts (Guilminot, 2012). The reduction process employed a platinum rod as the anode. A synthetic felt pad was fixed onto the anode tip to avoid direct contact between it and the artifact. The cathodic potential of the artifact under treatment was imposed via a cotton thread tied around the electrolyte-soaked felt-tip, while the other end of thread was immersed in a beaker containing the same electrolyte and a reference electrode (Fig. 2A). The pad was soaked in the electrolyte and moved over the metal surface during cleaning (i.e. for reducing species). The pad can also be held on the region requiring stabilization (i.e. for extracting aggressive species such as chlorides). As the treatment progresses the pad becomes impregnated with polluting species (sulfur- or chloride-based) and as a result the treatment efficiency decreases and side effects are observed. On silver artifacts for instance, if polluting species are not removed from the electrolyte they cause re-tarnishing of areas that have just been cleaned (Fig. 2B).

More recently A. Pappot developed an innovative pencil for the local stabilization of active corrosion on chloride contaminated bronzes. This pencil ensures the continuous circulation of electrolyte to the metal surface with compressors and manometers placed adjacent to the supply and extraction tubes for the electrolyte reservoir (Pappot, 2012). The pencil consists of a glass envelope containing a
stainless steel tube as a counter-electrode (CE – anode) and an internal carbon fiber rod as a reference electrode (RE) (Fig. 3A). The cathodic potential of the object is maintained using the cotton thread (black) tied around the felt-tip. \( ^{1} \) The J. Paul Getty Museum, Los Angeles, Johann Ludwig Biller the Elder, Silver gilt stag (1660–1700), H: 66.5 × W: 27.0 × D: 21.9 cm (A). Re-tarnishing due to continued use of the polluted electrolyte during electrolytic reduction (B), \( ^{2} \) Atelier de l’Abbaye de Saint-Maurice.

Experimental

Our first prototype of the electrolytic pencil was directly inspired by Pappot’s pencil. In case of accidental leakage of electrolyte, we wanted to minimize the risk of alteration of wooden components. A slightly acidic (citrate buffered – \( pH = 4.8 \)) \( \text{NaNO}_3 \) electrolyte was chosen for this reason (Degrigny et al., 2002). This solution only has a cleaning effect while the object is being polarized, i.e. there is no inadvertent cleaning effect or staining by the electrolyte without electrolytic processes. The stainless steel counter-electrode was replaced by a platinum rod. The carbon fiber reference electrode was superseded by a vitreous carbon rod (0.06 V/Ag–AgCl) which was noted to be a more electrochemically stable material.

Prototype 1

The envelope of the first prototype was fabricated from poly(methyl methacrylate) (PMMA) tube, which is easier to machine and less fragile than glass. It contained the reference electrode, the counter-electrode, and a pair of tubes for electrolyte supply.
and extraction. These internal components were held apart in the lower end of the pencil envelope by cast silicone and in its upper end by a polyethylene (PE) cover; which the electrolyte circulation tubes and electric cables passed through. This configuration favored connectibility of the wires. However, it only provided a small and fixed (approximately 1.5 ml) volume inside the nozzle of the pencil fabricated as well by machining from PMMA (Fig. 4A). The pencil was designed so that revised nozzles could be inserted for evaluation. A plastic ferrule with an internal thread (Fig. 4A) was used to attach these nozzles and their pad (Fig. 4B), which is described next.

To ensure the nozzle conveys the electrolyte to the metal surface while preventing leakage, several materials for the pad were tested: a PVFM¹ (polyvinyl formal) micro-porous foam, a Levantine sea sponge, a cellulosic sponge, cotton fabric, and cotton wool. It was observed that the PVFM micro-porous foam provokes a shift in the potential during polarization. This is caused by the micro-sized pores (they account for approximately 90% of the volume) which – compared with more permeable sponges – partition the electrolyte and increase the overall resistivity of the material. Nonetheless, the PVFM foam was noted for its clear advantages over the other candidate materials: excellent mechanical robustness, easy to cut, suitable absorption, and retention of electrolyte. In the following, the area of the pad in contact with the metal surface is about 1 cm².

Several systems for circulating the electrolyte were considered and tested, including peristaltic pumps and diaphragm pumps. The latter were the most suitable since they are very precise and are particularly adjustable. During our testing of diaphragm pumps (SIMDOS 10, KNF®), we observed that optimal circulation was obtainable with two pumps: one for supply and another for extraction. They function in a closed circuit and are set so the apparent flow for extraction is slightly higher: \(+\sim 10\) ml/minute (Fig. 5). To dilute the extracted polluting species, the volume ratio of the electrolytic cell to the reservoir is \(1:\sim 1000\).

Prototype 2

The silicone joint above the electrolytic cell in prototype 1 was found to leak electrolyte internally into the envelope of the pencil, and the positioning of the electrodes and the circulation tubes was imprecise. A second prototype was developed to correct these problems. A moveable element made from PMMA and referred to as the piston was inserted inside a revised PMMA tube, which comprised the pencil envelope. The piston contained the electrodes and circulation

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¹This material is sold commercially as PVA (polyvinyl alcohol). PVFM always contains some PVA that makes the foam less chemically stable; trapping metallic cations (Ag⁺ and Cu²⁺). The most stable material we tested was AION® PVFM Clean Room Sponge (http://www.aion-kk.co.jp/en/products/absorption_clean_room_sponge.html, consulted on 22 November 2014).
tubes. An O-ring on the piston ensured it was readily adjustable and the electrolytic cell was internally leak-proof. Piston adjustments determined the volume of the electrolytic cell, the position of the electrode ends and the electrolyte circulation tubes (Fig. 6A). The volume of the cell ranged 1.5–3 ml. Investigations into the effects and optimization of the operating geometry of the electrolytic cell became possible.

Although the functionality of the second prototype proved successful during the cleaning tests of some Treasury artifacts (i.e. no leakage, no re-tarnishing, no H₂S evolution next to the pencil), it was insufficiently ergonomic. In particular, the plastic ferrule partially obstructed the operator’s observation during cleaning. Furthermore, the stiffness of the PMMA tube was uncomfortable to handle for extended durations. Lastly, the connections for the electric wires remained insecure (Fig. 6B).

Prototype 3

During conceptualization of the third prototype, it became clear that additional skills and resources were necessary to ensure the pencil could become ergonomic and accessible to the conservation-restoration field. As outlined next, collaborations with the Laboratoire de Recherches en Anthropotechnologie (EDANA) at HE-Arc Engineering, Neuchâtel and the Neuchâtel FabLab were established in an attempt to make this possible.

EDANA surveyed conservator-restorers in order to better understand the context, their body actions, and the daily sequence of their work. Identifying the behavior of conservator-restorers limited the potential for subsequent interference of their work-flow or the impediment of learning new work procedures.

The survey by EDANA also highlighted a skill that is inherent in all conservator-restorers: the capacity to build ad hoc tools from various resources for customized treatments of artifacts. This observation led us to fabricate the electrolytic pencil using a FabLab: a small-scale digital fabrication workshop. These workshops enable any visitor to build their own apparatus of any kind by using flat rate computer-controlled technologies; such as 3D printing, laser cutting, and digital milling. The sophisticated skills required to use these technologies are obtainable by conservator-restorers. The decision to use FabLabs for the third electrolytic pencil linked the conservation-restoration field to a large range of innovative resources for rapid prototyping (Jeanneret et al., 2014).

The fabrication technologies available in FabLabs completely modified the design and manufacturing process for the third prototype. The pencil was only assembled using parts made by laser cutting and 3D printing; as well as with commercially available components (e.g. electrodes, screws, and nuts). The materials and shapes of the fabricated parts were determined by the available machines. The field of 3D printing (or additive manufacturing) covers a large range of different techniques. The most accessible 3D printing technology consists of depositing layer by layer a thread of melted thermoplastic polymer (Fused Deposition Modeling) from a printer nozzle. The important parameters to consider are the precision of the nozzle movement, the size of the nozzle, and the minimum thickness of each layer (generally around 0.1 mm). This low-cost technique is available in all FabLabs. It was decided to fabricate most of the 3D printed parts for the pencil in colored or translucent polylactic acid (PLA). The FabLab in Neuchâtel uses the Ultimaker® 3D printer; an efficient machine from those available to the public. For laser cutting, the range of machines at FabLabs is larger. Fabrication by laser cutting is very accessible: from creating design files (cutting plans) to using the cutting machine. Different materials can be cut precisely into shape from sheets. Laser cutting is faster than 3D printing and is suitable for fabricating many small parts.

Figure 6 CAD of prototype 2 of the electrolytic pencil (A) and its evaluation on the foot of the Monstrance of Sainte Apollonie (twelfth-fourteenth century), Treasury of Saint-Maurice Abbey (B), ©Atelier de l’Abbaye de Saint-Maurice.
FabLabs also presented opportunities to address the eventual distribution of the pencil and its future development. Since the conservation field is a small and specialized market, it was considered more feasible to produce a tool which conservator-restorers could take ownership of and tailor according to their needs. It became essential to create a pencil which could also be fully demountable. In this way, conservators could eventually re-make its components to improve or modify the intended functionality. The FabLab approach advocates the sharing of knowledge related to the available production methods. When an end-user wants to modify their design, they just need to produce a computer-assisted 2D or 3D drawing and visit their nearest FabLab. They can then fabricate new parts with the help of other FabLab users. These FabLabs are constantly evolving and are so far operating in several countries.

On the basis of considerations and information gained from the first and second prototypes, the third prototype was developed. According to our observations, discussions, and the decision to fabricate the pencil in a FabLab, the reformulated needs helped refine and prioritize the criteria for the pencil:
1. easy insertion/removal of electrodes;
2. demountable nozzle and easily replaceable pad;
3. observable electrolytic cell; and
4. adjustment of the electrolytic cell volume.

Since the method for circulating electrolyte using two diaphragm pumps and the integration of the counter and reference electrodes inside the pencil proved effective for prototypes 1 and 2, we retained these features. We also continued with the location of the electrodes inside an internal but now immobile structure, formerly referred to as the piston. We developed this new internal structure – referred to as the pencil core – around the predetermined dimensions of the commercially obtained electrodes and circulation tubes.

The pencil core for the third prototype was assembled from three black high-density polyethylene (HDPE) frames, which were slotted together using equiangular notches in the edges of a series of transparent PMMA discs. Both the frames and discs were laser-cut. The discs have holes for the electrodes and the electrolyte circulation tubes. The lower ends of the frames were inserted into notches in the head of the pencil core (Fig. 7A). The head was 3D-printed on a Creator B9® using a UV polymerizing resin (B9R-1-Red Resin). A pair of O-rings sit inside grooves around the head. One O-ring and the smooth surface finish of the groove ensure sealing against electrolyte leakage. The second O-ring mechanically retains the frames in place. The upper end of each electrode is secured inside a mandrel comprising a component scavenged from a commercially available mechanical pencil (Fixpencil by Caran d’Ache®). Each mandrel is openable using springs at the top of the pencil core. The envelope of the pencil is made from a series of laser-cut notched black

Figure 7 Close-up views of the lower section of the pencil core comprising the HDPE black frames, the PMMA discs, the B9R-1-Red resin head and the electrode mandrels (A); the envelope inserted in a PVDF heat-shrink tube (B); and the translucent PLA cover and the black PLA push-button for releasing the electrode mandrels (C).
HDPE rings and frames. The structure of the envelope is enclosed and constrained by a transparent polyvinylidene fluoride (PVDF) heat-shrink tube (Fig. 7B). The pencil core slides inside the envelope. The upper part of the pencil is referred to as the cover. It is made from translucent 3D printed PLA and is fixed to the pencil core with screws. The upper ends of the frames of the envelope are attached to the cover using O-rings in notches. The cover features a black 3D printed PLA push-button for opening the electrode mandrels. A braided sleeve containing both the electrolyte circulation hoses and the electric cables passes through the cover (Fig. 7C).

The nozzle is attached to the lower ends of the frames of the envelope using the O-ring and notch method used with the cover. It was 3D printed with translucent PLA. A series of laser-cut black HDPE rings can be inserted between the lower part of the envelope and the nozzle to extend the volume of the electrolytic cell. The volume of the cell ranges 1.5–3 ml. Teeth in the tip of the nozzle retain the pad. The fully assembled pencil is in Fig. 8A. Fig. 8B shows a cross section of the nozzle and pencil core including the locations of the electrodes and the electrolyte circulation tubes. This third-generation electrolytic pencil is called the Pleco, after the fish which cleans aquariums (http://fr.wikipedia.org/wiki/Hypostomus_plecostomus).

**Electrochemical measurements**

Voltammetry (i.e. measurements of current against potential applied) and chrono-amperometry using a potentiostat (OrigaLys®, Origastat e200) were performed to assess the behavior of the electrolytic pencils. This step was taken to verify whether the electrolytic reactions were the same as those which occur during full immersion, and whether their potentials differed. Two devices were used: a so-called drop cell and the Pleco. Their electrolytes were citrate buffered NaNO₃ 1% by weight, pH = 4.8. Linear voltammetry was performed in the cathodic field, starting at Ecorr (or the open-circuit potential), at a scan rate of 10 mV/second. The surface area investigated was 1 cm².

For the drop cell, a Ag–AgCl reference electrode (Metrohm®, ref 60726100 6.0726.100) held with a retort stand and clamp was inserted in a junction tube containing the electrolyte. This configuration prevents contamination of the buffered NaNO₃ electrolyte by the KCl electrolyte inside the reference electrode; without modifying the potential of the reference electrode (0.21 V/Standard Hydrogen Electrode – 0 V). A drop of buffered NaNO₃ electrolyte was placed between the surface of the metal object (working electrode) and the porous plug in the junction tube. For the counter-electrode a platinum wire was inserted into the drop of electrolyte. This configuration formed a three-electrode cell (Fig. 9). The drop cell device is very similar to the configuration of an electrolytic pencil, except that the three...
electrodes are closer to each other and they directly contact the electrolyte (ensuring no ohmic drop). It is as well the closest device to electrochemical measurements by immersion.

Prior to taking electrochemical measurements, the surfaces of the objects considered for investigation were degreased with ethanol to remove exogenous particles and analyzed using a portable X-ray fluorescence spectrometer (NITON XLt 950 Air GOLDD+ analyzer, ThermoFischer®). This was performed because significant variations in the composition of silver alloys affect the potentials required to reduce tarnish (Degrigny & Witschard, 2006).

Results
To ensure the different prototypes were adequate for particular conservation requirements, they were systematically evaluated on some tarnished silver on artifacts from the Treasury of Saint-Maurice Abbey. They were assessed in terms of their electrochemical behavior and practical aspects, such as artifact safety and ergonomics.

All XRF investigated and subsequently cleaned silver sheets were determined to comprise either a silver-copper alloy (Cu content: 1–14% by weight), and small percentages (less than 1% by weight) of lead (Pb) and gold (Au) were found in medieval alloys. These XRF results are consistent with those obtained during prior analyses of the metallic parts of the shrine of Saint Sigismond and his children (Degrigny & Witschard, 2006).

Since leakage of electrolyte occurred while using prototype 1, it was only tested on entirely metallic objects. Results are not reported in this paper.

Defining treatment parameters
First the parameters of the electrolytic cleaning process were defined by linear voltammetry using the drop cell, as previously depicted in Fig. 9. Fig. 10 shows the wider experimental configuration with the object (working electrode) under cathodic polarization. Electrical contact was made using an aluminum strip attached to the object with adhesive tape (red arrow). Measurements were taken in static mode, i.e. while the configurations were secured by retort stands and clamps.

The potential of the tarnished metal was scanned cathodically from Ecorr (0.23 V/Ag–AgCl) to −1.5 V/Ag–AgCl. The voltammetric plot obtained (Fig. 11) shows two reduction peaks, commencing at about 0.1 V/Ag–AgCl for the first (I) and at about −0.7 V/Ag–AgCl for the second (II). These peaks respectively correspond with the reduction of AgCl to Ag and with Ag₂S to Ag (Degrigny & Witschard, 2006). Their maxima – at which chrono-amperometric polarizations are often carried out to speed up reduction – are situated at about 0 and −1 V/Ag–AgCl.

Secondly, we investigated how the previous parameters varied between the electrolytic pencils. To compare the data from the drop cell and the second pencil prototype, voltammetric plots were acquired from a seventeenth century gilded silver candlestick.
(Fig. 12). Measurements were again taken in static mode. To enable comparison, the plots presented in Fig. 13 are given versus the vitreous carbon reference electrode (0.06 V/Ag–AgCl).

The open-circuit potential of the candlestick with the drop cell is situated at about 0.19 V/vitreous carbon, while it is around 0.08 V/vitreous carbon for the prototype 2 pencil (Fig. 13). It appears that without cathodic polarization, the prototype 2 pencil induces a lower corrosion potential (by about 0.1 V) compared with the value obtained using the drop cell. This phenomenon is partly due to the heterogeneity of the surface tarnish on the gilded silver candlestick and the ohmic drop caused by the micro-porous pad in the end of the pencil.

The maxima of reduction peaks I and II acquired by the drop cell are shifted when compared with those in Fig. 11. For the reduction AgCl→Ag the potential is shifted negatively from −0.06 to −0.3 V/vitreous carbon and positively from −1.06 to −0.86 V/vitreous carbon for the reduction Ag2S→Ag. These results indicate that the tarnish due to prior handling of the candlestick is more prominent, causing a larger AgCl→Ag peak, than for the tarnish on the front plate of the reliquary head of Saint Candide. Conversely the tarnish due to atmospheric sulfur species is less on the candlestick than on the reliquary head. As mentioned before, these results clearly demonstrate how the cathodic potentials required to remove tarnish (maxima of the reduction peaks) depend on the amounts of AgCl and Ag2S.

The prototype 2 electrolytic pencil induces large fluctuations in current due to the pumping of the electrolyte. This modifies the volume of electrolyte on the metal surface due to its absorption and extraction. Furthermore we noted that the potentials of the maxima of reduction peaks I and II were shifted towards more negative values, respectively −0.6 and −1.25 V/vitreous carbon. This shift is once again due to the differences in tarnish on the surface of the gilded silver candlestick and the ohmic drop caused by the pad in the pencil.

To better discern the shifting of the reduction maxima, but this time with the Pleco, linear voltammetry of the front plate of the reliquary head of Saint Candide was performed in static mode (Fig. 14); secured likewise as with the drop cell (Fig. 10). While using the Pleco the current fluctuations were lower than with the prototype 2 electrolytic pencil (Fig. 13), indicating a less erratic circulation of the electrolyte (Fig. 15). We again observed the same shift in direction of the maxima for reduction peaks I and II, but this time towards even more negative values as presented in Fig. 11, respectively −0.6 V/vitreous carbon for AgCl→Ag and −1.75 V/vitreous carbon for Ag2S→Ag (Fig. 15).

**Electrolytic cleaning with the Pleco by chronamperometry**

Once the potentials required to effect electrolytic reduction were defined, cleaning was performed in successive steps. The tarnish comprising AgCl was...
reduced first. It was followed by the reduction of tarnish comprising Ag₂S. To speed up the reduction of AgCl on the area investigated on Figs. 10 and 14, we imposed a potential of \( -0.9 \text{ V/vitreous carbon} \), far beyond the maxima of reduction peak I, but before the start of reduction peak II (Fig. 15). During cleaning the operator moved the Pleco over the surface of the metal: dynamic mode (Fig. 16).

While applying a constant cathodic potential, the reduction current decreased continuously toward a stable value after a few tens of seconds. This process was reproduced for each successive position of the Pleco on the tarnished surface. Cleaning took longer on areas worked in relief (Fig. 17A), when compared with smooth upper surfaces. As can be seen in Fig. 18, the target current for the relief was not obtained after 30–40 seconds (the first four positions of the Pleco), whereas the target (\(-1 \text{ mA/cm}^2\)) was reached after only 20–25 seconds for the smooth surfaces (the last six positions of the Pleco). The cleaned surface was rinsed with deionized water on cotton swabs.

The reduction of Ag₂S on the same surface was carried out afterwards at a potential of \(-1.75 \text{ V/vitreous carbon}\). The same approach as before was applied. There was minor evolution of H₂S. After
fully cleaning the silver tarnish, the surface was again rinsed with deionized water. Fig. 17B shows the cleaned surface of a detail of a relief on the front plate of the reliquary head of Saint Candide.

Overall, we observed that the Pleco in static mode enabled, like the drop cell, determination of the type (AgCl and/or Ag₂S) and amount of tarnishing on a local area of metal. It also enabled determination of the optimal cleaning parameters, i.e. the potentials of the maximas of the reduction peaks; and the duration of electrolytic cleaning. After defining these treatment parameters, the Pleco was used in dynamic mode to clean the corresponding surface.

The Pleco is considered safe for the object since there is no leakage of electrolyte, even for areas in relief. Meanwhile, it cleans efficiently since we apply adequate potentials to properly reduce the silver tarnish (AgCl and/or Ag₂S). More importantly, the operator fully controls the level of cleaning. The pencil can also be removed at any moment from the metal surface.

Conclusion

The development of the electrolytic pencil for local cleaning of silver tarnish required several steps. The first prototype achieved effective and safe circulation of the electrolyte by using a pair of diaphragm pumps. The second prototype benefited from various improvements in the watertightness of its electrolytic cell and the positioning of the electrodes inside the pencil. The pad enclosing the electrolytic cell was investigated in order to control its effect on the treatment parameters defined with the drop cell. From the materials tested, the micro-porous polyvinyl formal foam performed the best.

The collaboration with the EDANA unit of HE-Arc Engineering enabled us to continue developing the electrolytic pencil by including ergonomic aspects that are rarely considered in such a research project. The actual philosophy behind the fabrication of the pencil changed tremendously and the wish to make a low-cost and open source tool that can be optimized by end-users fostered our collaboration with the FabLab in Neuchâtel. Laser-cutting and 3D-printing technologies led to the development of an innovative electrolytic pencil called the Pleco.

Following its assembly, the Pleco was validated during the local cleaning of silver tarnish on some areas of the masterpieces in the Treasury of Saint-Maurice Abbey. We observed that the Pleco is a versatile tool, for both evaluating the type and amount of tarnish required to define the electrolytic cleaning parameters, and to actually perform local cleaning. It is planned to use the pencil to treat composite artifacts which comprise variously tarnished plates. The aim will be to determine the duration of the tarnish characterization and removal processes, as well as practical aspects concerning the saturation of the pad and the pollution of the electrolyte reservoir.

It is expected that future versions of the Pleco will feature improvements. While the initial objective was to develop a low-cost tool, the diaphragm pumps, as well as the platinum and vitreous carbon electrodes are rather expensive. More affordable alternatives are being considered. Technical aspects requiring further investigation include the nature of the electrochemical reactions due to the PVFM pad and the way the volume of the cell is affecting them. Some instability of the reference electrode signal during polarization also requires attention.

The Pleco has its dedicated webpage (http://www.fablab-neuch.ch/pleco). The fabrication files and the Pleco assembly and installation instructions can be downloaded free of charge.

Our wish is that this open source tool will benefit from improvements brought by its future end-users. The forum of the Pleco webpage aims to provide a platform to all those who are willing to contribute and share their experiences with the Pleco in ways that the heritage conservation field considers best.

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