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Selective Electrochemical Treatment of Naturally Aged Silver Alloy Artefacts

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ABSTRACT

Conservation interventions on silver tarnish and corrosion layers include mechanical, chemical, and electrolytic techniques. Electrolytic reduction is still disputed among metal conservators. The prevailing conviction with many is that mechanical cleaning methods are more likely to maintain control over the result than electrochemical methods. A survey on this subject undertaken in Germany and Austria suggested that this may be due to the traditional approaches of academic education. An electrolytic pencil was further developed and has been applied on naturally aged silver artefacts of the nineteenth and twentieth centuries. The influence of the electrochemical potential difference between artefact and counter electrode as well as of the tip diaphragm material was evaluated. A minimized material loss and a good controllability of conservation interventions on silver alloys were demonstrated.

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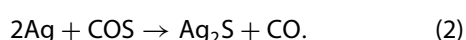
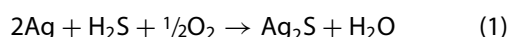
KEYWORDS

Electrochemical treatment; electrochemical pencil; naturally aged silver; tarnishing; conservation practice; survey

Introduction

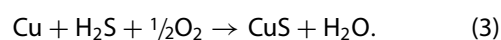
Silver (Ag) has always been highly valued. It has often been used for the production of decorative objects because of its beauty. As a precious metal, Ag exhibits a superb chemical resistance and can be excellently worked and shaped mechanically. However, pure Ag is too soft for practical use, which is why it is often alloyed with copper (Cu). These Ag–Cu alloys are used in a wide variety of applications, from jewelry, silver tableware, medals, coins, to other arts and crafts, or industrial products. Also frequently, Ag has been used as a coating material.

One of the most valued properties of Ag is its high metallic gloss, which is usually short-lasting depending on the pre-treatment. Ag tarnishes, generated by the conversion of Ag to silver sulphide (Ag₂S) under the influence of sulphur (S) compounds from the air. Articles of daily use are contaminated with other impurities by handling. Depending on their thickness, the tarnish layers can be yellowish-brown to blue–black in color (Kutzelnigg 1932). Inhomogeneous tarnishing associated with staining impairs the aesthetic appearance of an object. Ag can react with air pollutants such as hydrogen sulphide H₂S and carbonyl sulphide COS yielding Ag₂S (Rice et al. 1981; Franey, Kammlott, and Graedel 1985; Graedel et al. 1985; Graedel 1992):






Since most Ag objects were made of Ag–Cu alloys, or the

Ag served as a precious metal coating, divers element compositions must also be considered in terms of the material properties and aging phenomena. Thus, the conversion of Cu may also take place (Rice et al. 1981; Weichert et al. 2004; Knotková and Kreislová 2007):



Ag and Cu can be alloyed with many metals. Besides Cu, Ag can be alloyed with gold (Au) or palladium (Pd). Copper can also be alloyed with zinc (Zn), tin (Sn), lead (Pb), and nickel (Ni). Depending on the composition of the alloy and the melting temperature of the individual components, a wide variety of phase distributions and structures can be created in the solidified metal (Costa 2001). Factors such as the individual corrosion potential, environmental influences, manufacturing techniques and surface roughness, material wear, temperature, and the duration of exposure affect the corrosion behavior of the alloys (Franey, Kammlott, and Graedel 1985; Graedel 1992; Letardi 2013; Cieslewicz and Schweitzer 2017; Paysan 2017). The respective sulphide tarnish layers coexist with oxide phases. They can be porous or dense with more or less good adhesion to the surface. Uniform oxide and sulphide layers are rarely formed. On naturally aged surfaces, they are usually irregularly distributed and vary in thickness.

In the case of Ag alloys with Cu, copper compounds also occur in Ag corrosion conversion layers. Increased H₂S and COS concentrations, dust, food, and cleaning agent residues and moisture promote corrosion processes, especially on objects of everyday use. Salt-polluted soils lead to the formation of silver chloride

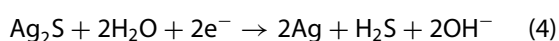
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(AgCl), a white crystalline substance which darkens under the influence of light due to the photochemical reduction of Ag by the chloride. In acidic soils, copper components are dissolved from the silver alloy over time, which can cause grain growth of the silver crystallites and lead to embrittlement of the alloy (Krehon 1991; Ottenwelter 2014).

Conservation professionals therefore apply a variety of tarnish removal methods with the aim of re-establishing the original aesthetic appearance and luster of silver based on the passivation with transparent Ag oxide (Plenderleith and Werner 1972; Krehon 1991; Costa 2001; Palomar et al. 2016a). Various aspects, guided by a thorough examination of the object and its environment, the state of preservation and aging, its history but also the future use and placement, contribute to the decision-making process of conservation and preservation measures. They involve the evaluation of the need for treatment and protection of the artefact (Krehon 1991; Costa 2001). Established methods of tarnish treatment for the preservation of historical Ag artefacts include mechanical removal (Glenn Wharton, Maish, and Ginell 1990) using abrasive pastes and tools, divers forms of saponin like soap root (dried and shredded root of the *Saponaria officinalis* plant) decoction or the boiling of soap-nuts (fruits of the plant *Sapindus mukorossi*) (Krehon 1991; Hawkes 2016), as well as chemical removal including acidified thiourea-based silver dips that effectively dissolve tarnish constituents (Contreras-Vargas, Ruvalcaba-Sil, and Rodríguez-Gómez 2013; Hawkes 2016). More seldomly, laser (Kautek 2010; Angelini et al. 2016; Palomar et al. 2016b) or plasma (Negri et al. 2011; Grassini 2013) cleaning is carried out.

Electrochemical methods have gained practical significance in the treatment and analysis of tarnish layers (Macleod and Neil 1979; Degriigny et al. 1996; Doménech-Carbó, Doménech-Carbó, and Costa 2009; Degriigny 2010; Letardi 2013). The need of a selective electrochemical treatment of inhomogeneously naturally aged Ag artefacts led to the development of electrolytic pencils (Aldaz et al. 1986; Degriigny et al. 2016; Hoffmann 2016; Paysan 2017; Erny, Degriigny, and Menart 2018). This approach consists in the electrochemical reduction of the corrosion product of Equation (1) (Novakovic, Vassiliou, and Georgiza 2013):



The simplest approach is the submersion of the Ag artefact as working electrode into the electrolyte as a cathode. When the current is monitored, its decrease can indicate the completed conversion (Graedel 1992; K. Leyssens et al. 2004; Degriigny 2010). Analogously to Ag, pure or alloyed Cu surfaces can also electrochemically be reduced:



In common parlance, but also in the literature, the chemical dissolution, mechanical removal, as well as the electrolytic or plasma-technical reduction of corrosion products are universally referred to as ‘cleaning’. Since the corrosion products are definitely not external impurities such as soiling or dust, but converted substrate materials, it is in fact misleading to speak of ‘cleaning’ in this context. Electrochemical reduction can be considered as a technique of re-conversion to the original surface state of the metal.

In the present work, the state of the art was compared with the results of a survey of the feedback of metal conservation professionals experienced in the treatment of Ag artefacts. Twelve colleagues were ready to respond to the inquiry. Furthermore, the electrolytic reduction of Ag₂S tarnish layers with a pencil is described. A custom-made electrolytic pencil was developed in order to achieve a dedicated tool that is as small and handy as possible to enable the treatment of finely shaped and deep surface profiles. Its design was determined by the requirement of easy and fast changes of the tip diaphragm material, the free shaping of the tip geometry – such as narrowly pointed or flat and broad, and a diaphragm holder for an easy-to-manufacture and electrolyte-tight diaphragm geometry. Moreover, an important criterion of the pen design was the quick and practical replacement of the diaphragms in order to study the contamination and the wear of the tips depending on the treatment time and the working pressure. Electrolytic treatments were carried out with the main intention of assessing the suitability of the developed electrolytic pencil for the use in conservation practice.

Experimental

Methods

A customized electrolytic pencil for the electrochemical treatment with potential control of metallic artefacts was designed and manufactured (Figure 1). Various membrane tips were attached to a glass cylinder ($l = 11$ cm, internal diameter = 1.3 cm) by a copolyester (CPE) tip mounting (Figure 2). The opposite side of the cylinder was closed with a rubber cap accommodating the electrolyte inlet and outlet silicon tubes and the insulated electric supply lines for the counter electrode (CE) and the reference electrode (RE). The counter electrode consisted of a gold rod ($l = 4$ cm, diameter = 1.5 mm), and the reference electrode of a graphite rod ($l = 4$ cm, diameter = 2 mm, Faber-Castell Fallmine TK 9071 3B). This material was submersed in a solution consisting of 0.1 M NaNO₃. A CH₃COONa/CH₃COOH mixture was added to serve as buffer resulting in a pH of 4.5. The potential of the reference electrode and its stability was measured versus a saturated Ag/AgCl electrode

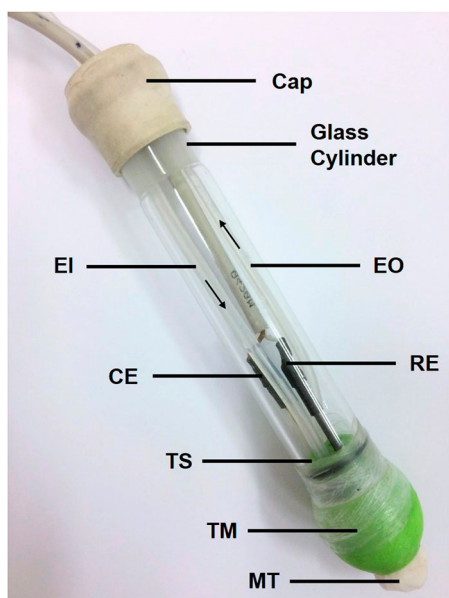


Figure 1. Electrolytic pencil. Glass cylinder fitted with a rubber cap. EI: electrolyte inlet. EO: electrolyte outlet. CE: counter electrode. RE: reference electrode. TS: tube sheet. TM: tip mounting. MT: membrane tip.

(+0.20 V vs. the Standard Hydrogen Electrode, SHE) over a period of 9 days to be at 0.20 ± 0.08 V (i.e. +0.40 V vs. SHE). In the context of this work, potentials are given vs. the graphite reference electrode.

The CE and the RE and the electrolyte tubes were held in position by a co-polyester (CPE) tube sheet near the tip mounting. Both the tube sheet and the various tip mountings were manufactured by 3D printing (Ultimaker2 3D printer and Ultimaker2 CPE printing material). The tube sheet was sealed against the glass cylinder by two O-rings (fluorine rubber). Two tip mountings with differently sized openings for the various diaphragm tips were manufactured by 3D printing. Electrolyte circulation to and from the electrolytic pencil (Figure 1) was maintained by two silicone tubes (external diameter = 3 mm) connected with an electrolyte supply (EI) and a collecting tank (EO). An external peristaltic pump (Mini-S 420, Ismatec) was installed between the electrolyte supply tank and the pencil. The object assumed the role of the working electrode (WE) (Figure 3). This three-electrode setup was controlled by a potentiostatic system (760C, CH

Instruments). Two diaphragm tip materials were tested. One was manufactured from a polyvinyl formal (PVFM) sponge resin (AION Clean Room Sponge, IAB Reinraum-Produkte GmbH, Braunschweig, Germany), and the other was a polyester felt tip (TIFOO GalvanoPen, MARAWE GmbH & Co. KG, Regensburg, Germany).

The surface of the cleaned spots was examined by optical microscopy (Olympus IMS STM-MJS). Energy-dispersive X-ray (EDX) analysis was done in a scanning electron microscope (SEM; ZEISS Supra 55 VP12). The effect of two contacting materials on the sample surfaces as well as the overall effectiveness of treatments with regard to uniformity and homogeneity on various natural surface conditions were studied.

Artefacts

Electrochemical conversion tests of naturally tarnished Ag surfaces were carried out on a spoon (Figure 4) and a pair of sugar tongs (Figure 5). The engraving 'AM 1861' on the spoon suggests a production year of 1861 (Figure 4). The hallmark '12' on the silver tongs represents an alloy with 12/16 or 75% by weight Ag and 25% of another metal normally Cu. The object can be dated before 1888 because the German ratio 'Lot' was replaced by the French ratio 'Promille' (thousandth) in 1888. One experiment was also run at a commemorative silver coin of the Österreichisch-Alpine Montangesellschaft 1881–1973 (Figure 6).

Results and discussion

Survey on the application of electrochemical methods in metal conservation

An application-oriented survey was designed to explore the acceptance and frequency of adoption of electrochemical methods in metal conservation practice, and in particular of an electrochemical pencil. It was distributed by the Österreichischer Restauratorenverband (ÖRV, Austria) and the Verband der Restauratoren (VDR, Germany) to all their registered conservators. Twelve colleagues responded to seven questions (Table 1).

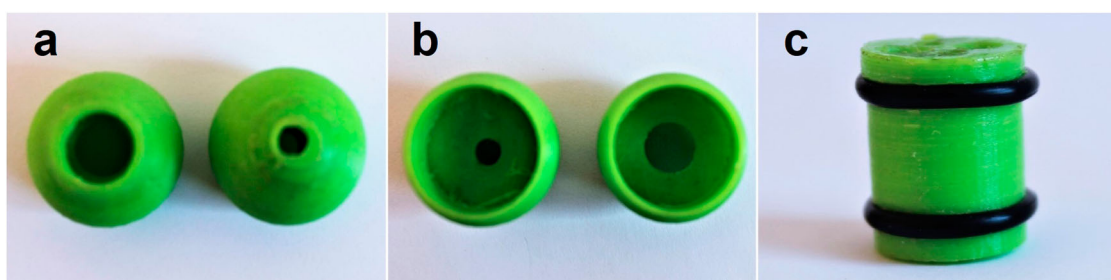


Figure 2. 3D printed components of the electrolytic pencil. (a) and (b) tip mounting with two different tip types; (c) tube sheet with two O-rings and two larger openings for the silicone tubes and two smaller openings for the electrodes (CE and RE).



Figure 3. Electrolytic pencil application at a silver spoon. The object is contacted as the working electrode.

- What methods/materials do you prefer for the treatment of corrosion layers on silver surfaces and why?

Seven out of twelve (~60%) respondents state that they work with electrochemical methods or have experience of this. Five conservators combined electrochemical methods with conventional cleaning methods using various abrasive powders such as chalks and soap root decoction. Five respondents (~40%) avoid electrochemical methods or do not use them at all.

- How satisfied are you with the common treatment methods? Have there been cases where you would have preferred a better result? What was the reason for that?

In general, respondents reported their dissatisfaction with the uniformity of the results achieved with

all treatment methods. The main difficulty for all methods consists in narrow recesses or hard to reach locations. Electrolytically treated surfaces require a mechanical post-treatment because they appear dull. Abrasive methods, on the other hand, are not sufficiently selective and leave residues, their removal rate is difficult to control, and the surface structure of the object gets densified.

- Do you have experience in the application of electrochemical treatment methods on metal objects? If so, which ones?

Ten out of twelve respondents (>80%) state that they had at least some experience with electrochemical treatment methods. Four (~30%) stated that they had gained electrochemical experience during their studies or internships.



Figure 4. Naturally aged silver spoon 'AM 1861'.



Figure 5. Naturally aged silver tongs. (a) untreated; (b) treated with the electrolytic pencil (electrolyte with pH4.5) equipped with the clean room sponge tip, at -2.5 V for 20 min, and consecutively at -3.0 V for 5 min; (c) Additional treatment with the electrolytic pencil equipped with a felt tip at -4.0 V for 10 min.



Figure 6. Front and reverse of naturally aged commemorative silver coin of the Österreichisch-Alpine Montangesellschaft 1881–1973.

- What electrochemical equipment do you employ? Do you work with a two or three electrode system?

Six respondents (50%) stated the usage of two electrode systems. Only four conservators (ca. 30%) used a three electrode potentiostatic pen system. The pen systems employed included self-made types, a commercial two electrode pen plating system (Rhodinette, Wieland Edelmetalle GmbH, Pforzheim, Germany), and three electrode potentiostatic systems (PalmSens, Houten, The Netherlands).

- Do you use or have you used so-called electrochemical pencils in the past?

Eight respondents (~70%) had experience with electrochemical pencils.

- What electrolyte solutions do you work with at the electrochemical treatment of silver surfaces?

The following electrolytes were used: CH_3COONa , NaNO_3 , NaHCO_3 , NaCl , and buffered Na citrate. One respondent stated the exceptional usage of an obviously pure NaOH solution in a two-electrode set-up.

- What kind of absorbent material (textiles, sponges etc.) do you use as contact material at the silver surface during electrochemical cleaning with the pencil?

Pencil tip materials used were cotton wool and cotton wool pads, cleanroom sponge cloths (D-2, IAB Cleanroom Products), felt tips (Karl Fischer GmbH), and absorbent sponges cut from larger washcloths.

Table 1. Survey to explore the acceptance and frequency of adoption of electrochemical methods in metal conservation practice distributed to the conservators registered with the Österreichischer Restauratorenverband (ÖRV, Austria) [www.orv.at] and the Verband der Restauratoren (VDR, Germany) [www.restauratoren.de].

Respondents	What methods/materials do you prefer for the treatment of corrosion layers on silver surfaces and why?	How satisfied are you with the common treatment methods? Have there been cases where you would have preferred a better result? What was the reason for that?	Do you have experience in the application of electrochemical treatment methods on metal objects? If so, which ones?	What electrochemical equipment do you employ? Do you work with a two or three electrode system?	Do you use or have you used so-called electrochemical pencils in the past?	What electrolyte solutions do you work with at the electrochemical treatment of silver surfaces?	What kind of absorbent materials (textiles, sponges etc.) do you use as contact material at the silver surface during electrochemical cleaning with the pencil?
1	Soap root decoction, whiting chalk ^a , rouge	–	Yes. Treatment of lead corrosion	Pen plating system (Rhodinette 2, Wieland Edelmetalle GmbH), Selen dry rectifier (Langbein Pfannhauser, Wien), rectifier (old, producer unknown), none of the systems is used for silver cleaning.	Yes: Pen plating system (Rhodinette 2, Wieland Edelmetalle GmbH)	'I never clean silver in this way – this removes all sulfides and the age value of the objects gets lost'.	–
2	PU sponges (Deffner & Johann)	Cleaning of metal threads in textiles: mostly unsatisfactory, because of inhomogeneous results due to 3D surface	No	None	–	–	–
3	Champagne chalk and water ('no scratches')	[1]	No	–	No	–	–
4	Electrolytic cleaning with potentiostat, linear sweep voltammetry. 'Because I hope to work with as little material loss as possible. In the case of gold-plated silver to preserve surface structures (processing traces, etc.) as far as possible, which is not achievable by mechanical methods due to the subsequent compression'.	(a) Lack of visual control in case of gilded Ag objects. (b) Presumption of chemically active residues when using complexing agents. (c) Abrasives (chalk etc.) are not very selective and leave residues. (d) Compaction causes changes in the surface structure. (e) Presumption of micro-scratches with cotton wool or sponge.	Yes. (a) Electrolytic cleaning of Ag and gold-plated Ag with potentiostat and linear sweep voltammetry. Electrolytic pencil (acc. M. Paysan and Pleco), electrolyte bath with magnetic stirrer. (b) Simple power supply and electrolyte-soaked cotton swab on counter electrode. (c) Method with Al foil and saline solution.	Three-electrode system (PalmSens EmStat 3+). Reference electrode: saturated calomel or glassy carbon. Counter electrode: platinized titanium, gold, gold-plated stainless steel, or stainless steel.	Yes, (acc. M. Paysan and Pleco).	Sodium acetate, CH ₃ COONa (0.1 M). Sodium nitrate, NaNO ₃ (0.1 M). Sodium hydrogen carbonate, NaHCO ₃ (2%).	Cotton wool, cleanroom sponge cloth (D-2, IAB Cleanroom Products).
5	Soaked cotton wool. Whiting chalk solutions. Electrolytic (rarely, only on small or mixed surfaces)	Dissatisfied when cleaning very dark layers. Considerable abrasion during mechanical treatment. Remaining surface after electrolytic cleaning is not satisfactory.	Yes, but rarely. Therefore, lack of practice.	–	Yes	Sodium hydrogen carbonate, NaHCO ₃ .	Felt tips (Karl Fischer GmbH).
6	Electrolytic cleaning	Combination of electrochemical and mechanical treatment (whiting chalk). Oxidation of reduced Ag on gilded surfaces after electrochemical Ag reduction.	Yes. Immersion and local pencil application on Ag or gold-plated Ag objects.	Two-electrode system (gilding station, Rhodinette, Wieland Edelmetalle GmbH).	No. Use of stainless-steel tweezers with a cotton swab at the tip. 'Quick and easy handling'.	Reduction: sodium hydrogen carbonate, NaHCO ₃ ; Oxidation: sodium acetate, CH ₃ COONa.	Cotton swab for pencil applications. Otherwise treatment by immersion for uniform Ag ₂ S reduction.
7	Benzines, alcohols, soap root extract, complexing agents.	Older and thicker sulphide layers can be problematic. In these cases, application of mechanical abrasives are preferred.	Seldomly.	Power supply unit, two self-made stainless-steel electrodes.	Yes, 1–2 times so far.	NaCl solution (approx. 15%).	Absorbent sponges cut from larger washcloths.

8	Both electrolytic and abrasive (micropolish). Electrolytic method safest for the surface, but need after treatment. Micropolish can be applied locally (also under the microscope).	Problems with persistent areas: uncertainty with stronger mechanical pressure or higher current application.	Yes. During professional study, in the context of a project work with electrolytic pencils on Ag.	Two-electrode system. Electrolytic pencil with gold or platinum wire electrodes, soaked cotton wool tampons.	Yes, as part of a seminar. –		Cotton wool pads.
9	Soap root decoction, micro-fibre cloth and ethanol, titanium dioxide. 'In cases of gilded and/or profiled surfaces, a mechanical treatment is not recommended'.	Generally content.	Yes. Electrolyte bath and electrolysis pencil.	Three-electrode system with reference electrode (Pt or glassy carbon).	Yes.	Sodium nitrate, NaNO ₃ (0.1 M).	AION Sponge.
10	'I prefer a combination of electrolytic and mechanical cleaning (titanium dioxide, whiting chalk). Electrolytic cleaning is an ideal and time-saving method for cleaning all-metal objects ... In my pre-study period, I only cleaned the surfaces mechanically with whitening chalk, because this was the requirement. Since I was able to try out electrolysis, it seems to be a useful addition'.	Electrolysis optimal for objects that can be dismantled. Stronger gloss can be achieved by additional mechanical treatment.	Yes. Electrolyte bath and electrolytic pencil.	Two self-made electrolytic pencils at the academy of arts.	Yes. Self-made pencils with glassy carbon and platinum electrode.	Sodium nitrate, NaNO ₃ (0.1 M).	Clean room sponge
11	'I use electrochemical cleaning with moderate success for pure silver objects. I still clean plated objects in the conventional way (soap baths, etc.)'.	So far, no success with electrochemical cleaning methods on copper and copper alloys. In the case of silver-plated copper surfaces or silver objects with a high copper content, I find that copper-containing components often have a greater effect on the surface than silver compounds.	Yes. Application only on pure silver objects.	Power supply unit with a stainless-steel electrode.	–	Sodium hydroxide, NaOH solution.	–
12	Electrolytic reduction in the bath or with a pen (own development based on ideas of the team around C. Degryny). Reduction of the tarnish layer and subsequent oxidative removal of the metallic silver on gildings. Mechanical polishing with titanium oxide (slow removal > maintains the original matt finish) or Micropolish Alumina 0.05µm (fast removal with low scratch depth due to small grain size > generates higher gloss).	Immersion bath: post-corrosion due to badly washed-out chemical residues. Laser: pits at the impact points of the laser beam; discoloration around the impact points. Whiting chalk in combination with soap or tensides: green corrosion underneath the cleaning agent residues.	Yes. (a) Electrolytic reduction in the bath or with a pen (own development based on ideas of the team around C. Degryny). (b) Reduction of the tarnish layer and subsequent oxidative removal of the metallic silver on gildings.	Three-electrode system for bath and pen. PalmSens2 potentiostat, power supply units, voltmeter.	Yes, but unsatisfactory. Due to the lack of electrolyte flow, the edges of the treated areas are retarnishing.	0.1 M sodium nitrate buffered as required with 10 ⁻⁴ M sodium citrate / citric acid. For the buffer solution see recipe: Romain Jeanneret, Using the Pleco: Electrolytic Treatment of Metal Components on Artefacts; ICOM-CC_METAL2016	AION Sponge D-2 Article no.: 361003.

^aSchlämmkreide.
1. Eipper (2014).

The detailed results are collected in [Table 1](#). Some conservators reject the application of an electrochemical treatment and prefer the mechanical abrasion approach because they claim that the artefact would lose its value due to the total removal of the sulphide film. They explain that their mechanical treatment provides a better control on the extent of the removal.

Experiments with the electrochemical pencil

The naturally aged silver spoon ([Figure 4](#)) and tongs ([Figure 5a](#)) exhibited an inhomogeneous dark tarnish in the original untreated status. The contamination layers exhibited a significant higher abundance in the recesses of the surface. In contrast, the raised, and therefore more exposed areas, showed much less tarnish due to the frequent usage touches. The application of the electrolytic pencil equipped with the clean room sponge tip, at -2.5 V for 20 min, and consecutively at -3.0 V for 5 min, resulted in a partial reduction of the tarnish and contamination layers ([Figure 5b](#)) with a remaining dull appearance. Additional treatment, however, with the electrolytic pencil equipped with a felt tip at -4.0 V for 10 min improved the conversion result with an increase of metal luster ([Figure 5c](#)). Actually, cleaning of thicker tarnish phases requires more negative cathodic potentials (Leyssens et al. 2006; Degriigny and Witschard 2007; Degriigny, Jeanneret, and Witschard 2015; Degriigny et al. 2016). The monitoring of the current transients (Degriigny et al. 2016; Paysan 2017) was omitted because the criterion to end the application was left to the naked eye observation of the conservator.

The applied overpotentials are all well beyond the reduction potentials of the respective conversion layers such as Ag_2S . That clearly means that hydrogen evolution is a substantial side reaction as is common in aqueous galvanic praxis. If bubble formation in the extremely thin electrolyte layer between the diaphragm and the working electrode would have occurred, it would have been hidden behind the diaphragm tip. Hydrogen evolution is an established cleaning approach in electrochemistry both in fundamental research and in galvanic praxis. Therefore, one can assume that the formation of gaseous hydrogen from hydrogen *in situ nascendi* can support the cleaning process mechanically. Moreover, a high overpotential is required to overcome the series resistance of the oxidic and sulfidic passive layers. It is clear that thicker coating require higher overpotentials as is well reported in literature (e.g. Degriigny et al. 2016).

Decision making in a conservation process of naturally aged silver surfaces depends on various factors. These are the original application as well as the age of the object, but also often traditionally shaped demands related to its aesthetics after conservation treatment. For example, to emphasize the plasticity

of the surface, it is sometimes desirable to leave patina residues in the depressions. In this context, it turned out that the treatment time was not decisive for a satisfactory result. However, a reduction threshold below -3.0 V could be clearly identified.

Considering the above-mentioned criteria in conservation practice, and in order to achieve a thorough surface analysis before and after the intervention, SEM-EDX overlay images were chosen instead of EDX spectra of single spots. The EDX elemental maps of the untreated sugar tongs show clearly the inhomogeneous contamination distribution typical for naturally aged silver artefacts. Dominant elements, i.e. Al, Si, Cl, S ([Figure 7](#)), and Cu ([Figure 8](#)) can be associated with contamination phases containing oxidized Al and Si in the depression region, and the surface conversion

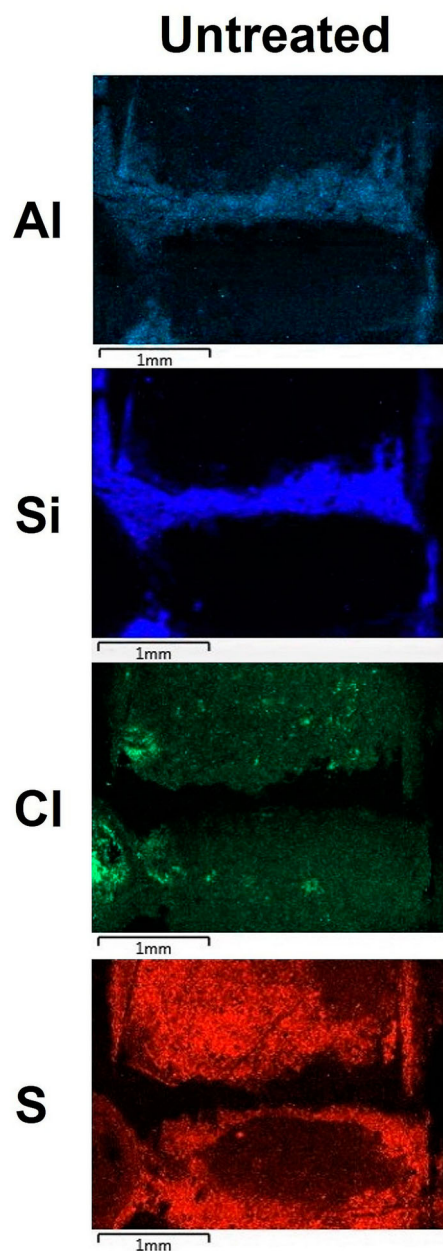


Figure 7. EDX analysis of a surface detail on a naturally aged silver tongs before the treatment with the electrolytic pencil.

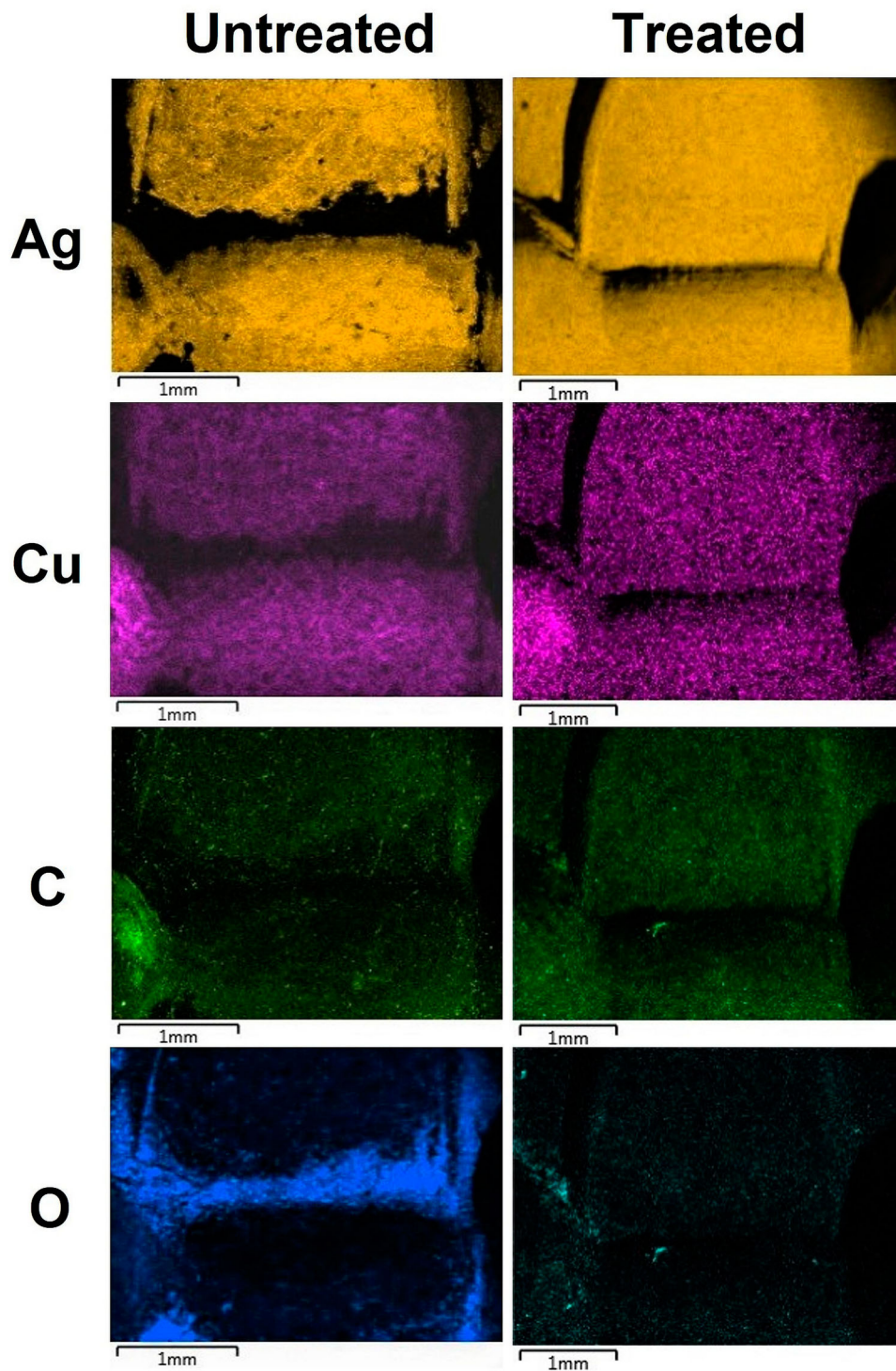


Figure 8. EDX analysis (Ag, Cu, C, O) of a surface detail on the naturally aged silver tongs before and after two steps of treatment with the electrolytic pencil (electrolyte with pH 4.5) equipped with the clean room sponge tip, at -2.5 V for 20 min, at -3.0 V for 5 min, and consecutively with a felt tip at -4.0 V for 10 min.

and corrosion by the formation of silver chloride and sulphide as well as copper sulphide and chloride on the plain elevated areas represented by Equations (1)–(3). On the other hand, contamination layers are indicated by C on the plain elevated regions, and O as a constituent of the above-mentioned oxidized Al and Si contamination phase in the depressions (Figure 8).

Figure 9 demonstrates the result of the electrochemical pencil reduction equipped with a clean room

sponge tip. It caused an extensive conversion of the sulphide phases to elemental Ag and Cu according to Equations (4) and (5). The pencil treatment eliminated the O signal in the depressions (Figures 8 and 9) suggesting the removal of the oxidic phases containing Al and Si. These were softened by the electrolyte. The mechanical contact action of the tip material with the artefact surface resulted in the subsequent removal depending on the applied pressure and the number of pencil strokes. An electrochemical aspect

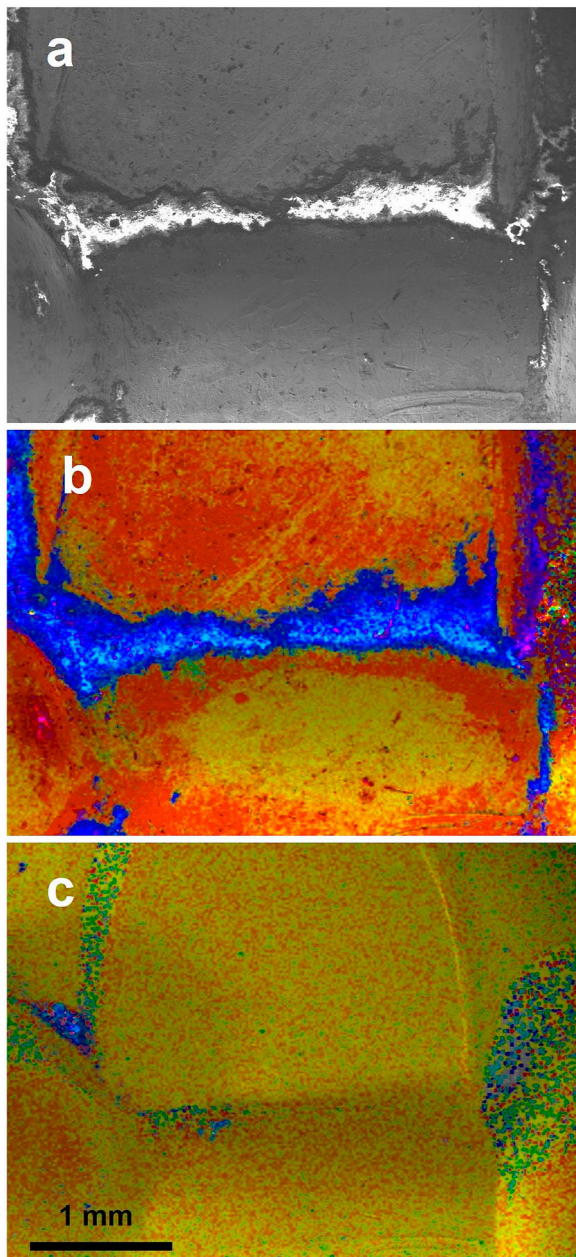


Figure 9. SEM image (a) and EDX analysis (overlay image of Ag, Cu, C, O, Al, Si, Cl, S) of a surface detail on a naturally aged silver tongs before (b) and after (c) two steps of treatment with the electrolytic pencil (electrolyte with pH4.5) equipped with the clean room sponge tip, at -2.5 V for 20 min, at -3.0 V for 5 min, and consecutively with a felt tip at -4.0 V for 10 min. Ag: yellow; Cu: purple; S: red; O: blue.

may be considered also. It is well known that the vigorous evolution of hydrogen gas bubbles during the reduction of electrode surfaces with high overpotentials can mechanically remove contaminants.

The nature of the tip material has a decisive influence on the cleaning result of the electrochemical pencil. Localized spot tests were carried out on the unstructured minted reverse of a naturally tarnished commemorative coin. **Figure 10** shows optical micrographs of two separate spots treated at -4.5 V. The potential was chosen more negative than the above-mentioned reduction threshold. Historical scratches

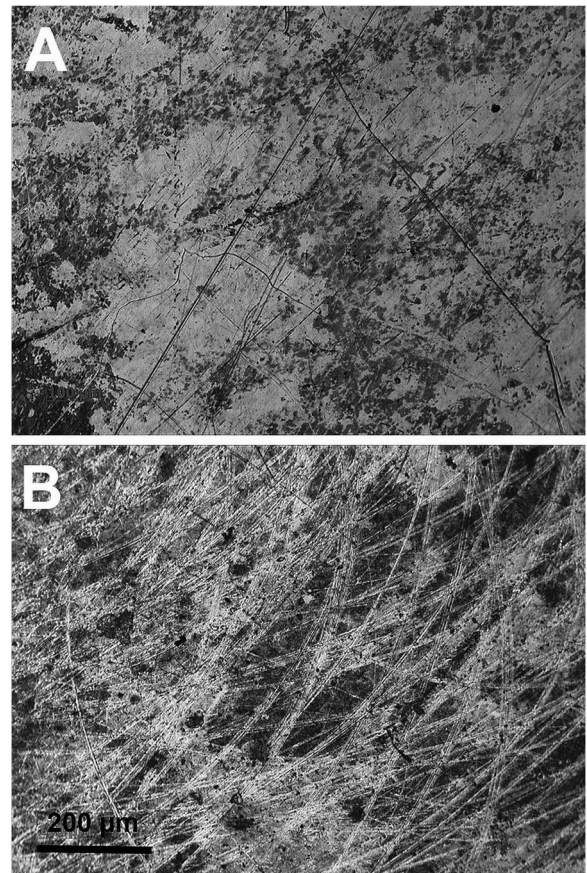


Figure 10. Surface quality in dependence of the tip material (optical micrographs), after electrolytic pencil treatments (electrolyte with pH4.5) at -4.5 V. (a) clean room sponge tip; (b) polyester felt tip. Substrate was the unstructured minted reverse side of a naturally aged commemorative silver coin.

appear dark, and none were added by the treatment with the clean room sponge material (**Figure 10a**). However, the felt tip diaphragm material caused significant scratch marks only after a low treatment time of 60 s (**Figure 10b**).

Conclusions

Electrochemical reduction can be considered as a technique of re-conversion to the original surface state of the material. The use of an electrochemical pencil on historical metallic artefacts has clear advantages over the more established techniques involving chemical and mechanical tarnish removal. The electrochemical intervention can avoid any material loss and allows much more control of the conversion results due to the chosen electrochemical parameters such as electrode potential of the artefact as working electrode, the current density, and the nature of the electrolyte.

As part of the presented research, metal conservation professionals experienced in the treatment of silver tarnish and corrosion in Germany and Austria were invited to participate in a survey about their experience with electrochemical methods. More than

80% of the respondents stated that they had at least some experience with them, and about 60% are regularly applying them. However, ca. 40% are completely avoiding electrochemical techniques. Ca. 40% of conservators are combining electrochemical with mechanical cleaning methods, and interestingly, about 70% had experience with electrochemical pencils.

Electrochemical conversion experiments of naturally tarnished Ag surfaces were carried out on a spoon, a pair of sugar tongs, and a commemorative silver coin. The self-made electrolytic pencil removed pollutant species such as chlorine and sulphur to a degree below the detection limit of the EDX analysis. The pen tip material, which functions as the electrochemical cell diaphragm, affected the intervention results, decisively. A felt tip caused scratches whereas the cleanroom sponge material produced no mechanical changes. The electrochemical pen is particularly suitable for treating localized corrosion and is a practical alternative to electrochemical treatment of artefacts merely by immersion in an electrolyte. Future electrochemical pencil studies on naturally aged silver alloys should consider long term monitoring in respect to surface conversion processes.

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