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# CLEANING OF SILVER GREAT MORAVIAN JEWELLERY BY POTENTIOSTATIC REDUCTION

Estelle Ottenwelter

Institute of Archaeology of the AS CR, Prague, v.v.i.  
ottenwelter@arup.cas.cz

Potentiostatic reduction was used to clean Great Moravian jewellery from Lumbe's garden cemetery, Prague Castle. These artefacts were covered by a thin tarnish layer. Polarisation plots, recorded directly on selected objects, and SEM/EDX analysis helped to identify corrosion products present in the tarnish layer and to set adequate parameters for treatment. Objects were successfully cleaned by electrolytic reduction at a constant potential in a sodium nitrate solution.

**ČIŠTĚNÍ VELKOMORAVSKÝCH STŘÍBRNÝCH ŠPERKŮ POMOCÍ POTENCIOSTATICKÉ REDUKCE** K čištění Velkomoravských stříbrných šperků nalezených na pohřebišti v Lumbeho zahradě Pražského hradu byla použita potenciostatická redukce. Tyto artefakty byly pokryty tenkou zčernalou vrstvou. Pomocí polarizačních křivek zaznamenaných přímo na vybraných předmětech a analýzou SEM/EDX byly identifikovány korozní produkty přítomné v této zčernalé vrstvě a nastaveny vhodné parametry ošetření. Předměty byly úspěšně vyčištěny za použití elektrolytické redukce v roztoku dusičnanu sodného při konstantním potenciálu.

## INTRODUCTION

As part of a three year project focused on research of the Lumbe's Garden cemetery (9th-11th AD) at Prague Castle, where the state elite linked to the princely environment of the early Czech state was buried, grave goods are being re-conserved (in the laboratory of conservation of the Institute of Archaeology of Prague) and investigated (in collaboration with the Institute of Chemical Technology). Among them, 188 silver jewels (temple rings, earrings, kaptorga, gombik) were recovered from the 141 excavated graves of the cemetery. Restored just after excavations in the seventies, with the available at that time methods, they underwent further restoration treatment in 2001. Past treatments using alkaline cyanide aqueous solution led to almost complete dissolution of corrosion products, and to severe leaching of the remaining metallic surface. Up to last year, the objects were stored in their original storage material (cardboard jewellery boxes), manipulated in many occasions for study and display and not protected from oxidants, pollutants and fluctuations of relative humidity. As a result they are highly fragmented and covered by a thin tarnish layer which alters the colour of their constitutional material and makes their identification difficult. For research, publication and display needs, these artefacts had to be re-restored. The conservation and restoration treatment goals aimed to increase legibility of the artefacts by joining fragments, consolidating the artefacts and providing safe storage. Removal of tarnish had to be performed on objects whose state of preservation allowed it for aes-

thetic and legibility consideration although these corrosion products are protecting the artefacts from further corrosion and although, they are situated in most cases under the limit of the original surface. The choice of method of cleaning was imposed by the necessity to choose a method which would remove exclusively the undesired superficial thin tarnish layer without loss of further metallic substrate and without risk of neither scratching the artefacts nor breaking them. These goals being more easily achieved by electrochemical cleaning than by mechanical and chemical methods [Costa, 2002, p.89.], potentiostatic reduction appeared to be the most suitable method.

## DESCRIPTION OF THE OBJECTS

In total, 50 objects were selected to be cleaned by potentiostatic cleaning. These objects are S-shaped temple rings (36 items) and earrings with rich granulation decoration (14 items) all dated from the 9th to the 12th century AD.

**S-shaped temple rings** are metallic open rings with a typical curly S-shaped ending. These ornaments were popular between the 9th and the 13th century in Central Europe. They were worn by women and children from all ranks of the society, attached to a fabric on the head, near the temples. Elaborated in plain copper alloys, silver alloys, gold or even iron according to social status of their owner, they were sometimes plated with tin, gold or silver [Ottenwelter – Děd – Hošek – Štefan, 2012 p. 526].

Most of them were manufactured from plain metallic wires. One end was hammered and bent to form an S-shaped end. Then the wire was bent to required form. Diameters of the temple rings and used wires varied in time.

Lumbe's garden temple rings, treated by potentiostatic reduction are all of small diameters, ranging from 12 mm to 15 mm. The thickness of the wire is ranging from 1.5 mm to 3.5 mm.

**Earrings with rich granulation work** These earrings were worn by upper class women and girls. They were most probably attached to a fabric on the head like the temple-rings. Their manufacture requires a high amount of silver and a higher technological level than the manufacturing of temple-rings.

They are formed with a central wire of round section for the upper part (the lock) hammered in square section for the lower part (the basket) on which decorative elements (rings, wires of different section and different size granules) are soldered. Two symmetric ornamental elements (the ears), formed by a row of granules between two rings, are decorating the central wire and a central ornament (the cluster), made of several juxtaposed rows of granules soldered on a small ring, is fixed on both sides of the central wire either with metallic strips [Čáp – Macháček – Špaček, 2001, p. 123–134] or soldered to it directly.

**Analysis of material** All the artefacts are made of almost pure silver containing a small amount of copper (below 5%) (Table 1). Temple-rings are made of silver alloys containing from 91 to 97% of silver and from 1.6 to 5% of copper, less than 1% of gold and less than 0.5% of lead. Five temple rings (H 103-10, H 104-6-8-9-10) are made of a silver-gold-copper alloy containing less silver (90%), more gold (5%) and about 3% of copper.

Předmět	Ag	Cu	Au	Pb
Temple-ring H 110-1	95,4	3,7	0,8	0,1
Temple-ring H 110-2	96,8	2,5	0,6	0,1
Temple-ring H 110-3	95,2	4,0	0,7	0,1
Temple-ring H110-4	95,4	3,7	0,8	0,1
Temple-ring H110-5	95,6	3,5	0,8	0,1
Temple-ring H 110-6	93,9	5,0	1,0	0,1
Temple-ring H 110-7	96,1	2,9	0,8	0,2
Temple-ring H 110-8	95,2	3,9	0,8	,1
Temple-ring H 110-9	94,9	4,2	0,8	0,1
Temple-ring H 110-10	95,1	3,9	0,8	0,2
Temple-ring H100-40	97	2,2	0,8	-
Temple-ring H100-41	96,1	3,7	-	0,2
Temple-ring H100-42	97,2	2,0	0,8	-
Temple-ring H100-43	96,8	2,4	0,8	-
Temple-ring H100-44	96,9	2,3	0,8	-
Temple-ring H100-45	96,3	2,8	0,9	-
Temple-ring H100-46	97,0	2,0	1,0	-
Temple-ring H100-47	97,1	2,1	0,8	-
Temple-ring H100-48	96,5	2,0	0,9	-
Temple-ring H100-49	97,0	2,2	0,8	-
Temple-ring H 103-3	94,1	4,4	1,1	0,4
Temple-ring H 103-4	94,0	4,6	1,0	0,4
Temple-ring H 103-8	93,9	4,5	1,2	0,4
Temple-ring H 103-9	93,4	5,0	1,2	0,4
Temple-ring H103-10	91,9	2,7	5,0	0,4
Temple-ring H 104-6	91,1	3,0	5,4	0,5
Temple-ring H 104-8	91,3	2,7	5,6	0,4
Temple-ring H 104-7	91,4	3,5	4,7	0,4
Temple-ring H 104-9	91,6	2,7	5,3	0,4
Temple-ring H 104-10	94,8	4,6	0,4	0,2
Temple-ring H 104-11	92,1	2,6	5,0	0,3
Temple-ring H 30-2	95,8	2,9	0,9	0,4
Temple-ring H 30-3	93,3	5,4	0,7	0,6
Earring H84-3	94,8	3,9	0,7	0,6
Earring H84-5	94,7	3,7	0,6	1,0
Earring H84-6	95,0	4,7	-	0,3
Temple-ring H84-7	98,0	1,7	0,2	0,1
Earring H84-8a	93,6	5,3	0,3	0,8
Earring H84-8b	97,0	2,5	0,3	0,2
Temple-ring H84-9	98,1	1,6	0,2	0,1
Earring H 89-3	96,8	2,3	0,3	0,6
Earring H 89-5	97,3	1,8	-	0,9
Earring H 89-6	96,5	2,8	0,2	0,5

Tab. 1 Results of X-fluorescence analysis (XRF) on surface of the selected artefacts, composition in wt%



Fig. 1 Example of earring and temples rings prior treatment, covered by a thin tarnish layer of variable thickness and color

The central wire and decorative elements of the earrings are made of almost pure silver with a low content of copper and traces of gold and lead. The content of copper is ranging from 1.8% to 4.7% with an average of 3% (Table 1).

The different elements were joined together by fusion welding using either crushed malachite mixed with an organic binder [Čáp – Macháček – Špaček, 2001, p. 34–36] or metallic copper, or silver-alloys fillings [Untracht, 1985, p. 350–351].

## STATE OF PRESERVATION

In the past, objects underwent chemical cleaning in aqueous solution of alkaline cyanides. As a result not only external corrosion products were dissolved but also metallic core leading to a substantial loss of material, leaching of the surface and in many cases loss of the limit of the original surface.

Up to last year, the objects were stored in original paper boxes, together with kitchen roll paper, obviously made of acidic and non-neutral material. No control of the environment and relative humidity were carried out. Furthermore, the objects were manipulated on many occasions during last decades undoubtedly without gloves. Therefore, they were contaminated with sodium chlorides, a major component of human perspiration, reacting with silver to form silver chlorides [Selwyn, 2004, p.138] as well as with grease and organic acids. As a result, they are covered by a thin layer of tarnish of variable thickness. The colour of the layers is varying from light yellow to black with iridescent films. In all cases, the tarnish is aesthetically displeasing and is disturbing the identification of silver (Fig.1).

The chosen artefacts have a good metallic structure contrary to objects manufactured with thin silver alloys sheets (gombik, kaptorga) which are almost completely mineralized. Temple S-shaped ends, being thinner and having gone through more intense cold working are subjected to stress-induced corrosion and are more brittle. Scanning electron microscopy shots revealed intergranular embrittlement, but considering the stress induced by mechanical cleaning, potentiostatic reduction was presenting less risk to the artefacts.

Some objects were broken and joined in the past. Degraded acrylic resin has spread onto the surface of many artefacts (Fig.1). Remains of degraded varnish are also visible on the temple rings.

## ANALYSIS ON CORROSION PRODUCTS

According to literature data, the principal component of tarnish films has been identified as acanthite ( $\alpha$   $\text{Ag}_2\text{S}$ ) but chlorargyrite ( $\text{AgCl}$ ) has also been identified as a major component. Chalcocite ( $\text{Cu}_2\text{S}$ ) can also be present in silver artefacts because silver alloys, as well as used solders, contain copper as a major alloying element [Costa, 2001, p. 22]. The associated species in the atmosphere are reduced sulphur gases, such as  $\text{H}_2\text{S}$ , and organic sulphur compounds such as carbonyl sulphides ( $\text{OCS}$ ) and dimethyldisulfide ( $\text{Me}_2\text{S}_2$ ) and  $\text{SO}_2$  [Costa, 2001, p. 21] as well as presence of chlorides ( $\text{Cl}_2$ ,  $\text{HCl}$ ) [Espíe-Lacoudre-Beldjoubi-Dugot, 2000, p. 20]. These pollutants are present in the atmosphere and can be found in higher quantities in indoors environments if material from which noxious gases evolve are present in the vicinity of the artefacts [Costa, 2001, p. 21].

SEM/EDX analyses performed on two temple-rings from the set have proved the presence of oxides, chlorides and sulphides (Fig.2).

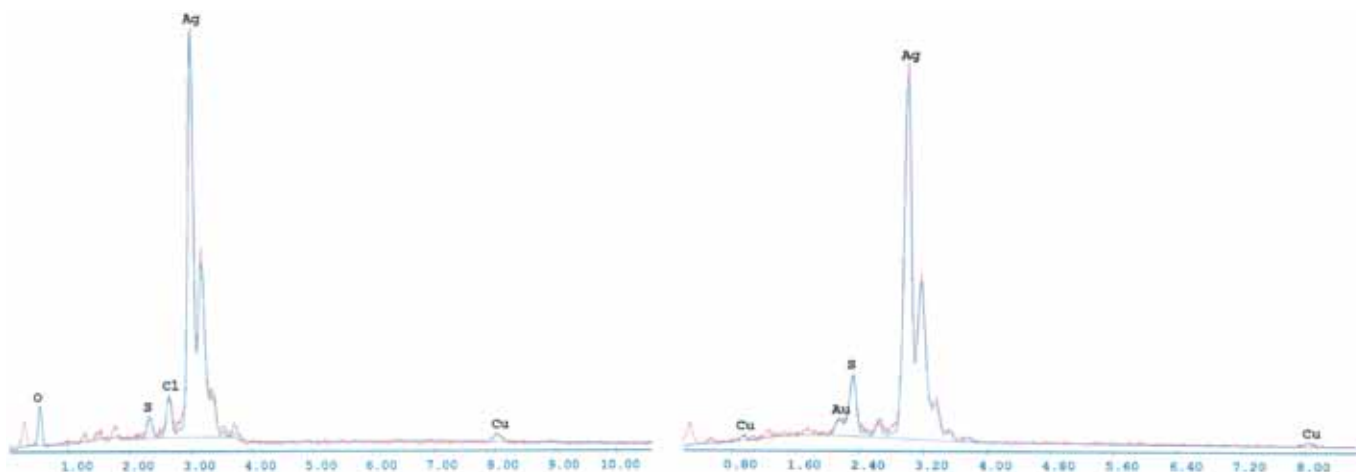


Fig. 2 SEM/EDX spectra of corrosion products present on two temple-rings before treatment

**Polarization curves** were measured for four representative objects with the aim to identify corrosion products present on the surface and to define the working conditions that should be used for the following treatment. Reduction peaks of compounds were identified in the plots according to waves current occurring at specific potentials in a given electrolyte.

According to authors, [Costa, 2002, p. 92; Costa, 2003; Costa – Dubu 2007, p. 2; Storme- Urban, 2011, p. 2], reduction peaks of silver sulphides products starts in 0.1 M  $\text{NaNO}_3$  electrolyte at -1.2V ( $\text{Ag}_2\text{S}$ ), in the case of pure silver. In the case of sterling silver, two peaks of reduction are observed. The first one starts at -1.2 V/ MSE and corresponds to the silver sulphides ( $\text{Ag}_2\text{S}$ ), the other starts at -1.6 V/ MSE and can be assigned to the reduction of copper sulphides ( $\text{Cu}_2\text{S}$ ).

The peak indicating silver chlorides reduction starts at -0.3 V/MSE [Costa, 2011, p.92; Costa 2003]. Reduction of silver oxides starts at -0.55 V/MSE (Costa-Dubu, 2007, p.2).

Reductions of oxides of copper ( $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ ) may start at -0.4V/MSE and -0.8 V/MSE (Costa, 2003).

Linear sweep voltammetry was performed on four representative artefacts of the set as an attempt to identify corrosion products present in the tarnish layer and to choose proper potential for the following treatment of the objects.

**Group 1:** Temple ring: Ag (96.8%, Cu 2.5%, Au 0,6%, Pb 0.1) (Fig.3).

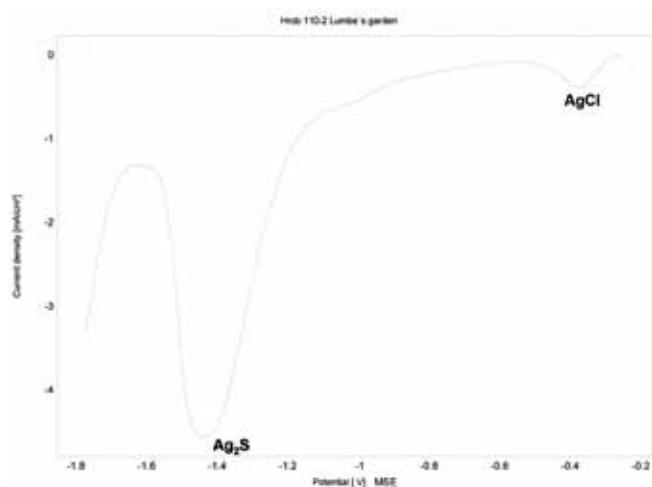


Fig. 3 Polarization plot recorded on a temple ring from group 1 (0.1 M  $\text{NaNO}_3$ , scan rate 10mV/s). The plot reveals presence of silver chlorides and sulphides respectively

The plot reveals the presence of peak of reduction of silver chlorides ( $\text{AgCl}$ ) starting at -0.3V/MSE with a maximum of intensity at -0.4V/MSE. A second peak of reduction corresponding to the reduction of silver sulphides starts at -1,2V/MSE with a maximum intensity at -1.45V/MSE. Hydrogen evolution starts at -1.65 V/MSE.

**Group 2:** temple ring with a lower content of silver and higher content of gold: (Ag 91.3%, Au 5.6%, Cu 2.7, Pb 0.4%) (Fig.4).

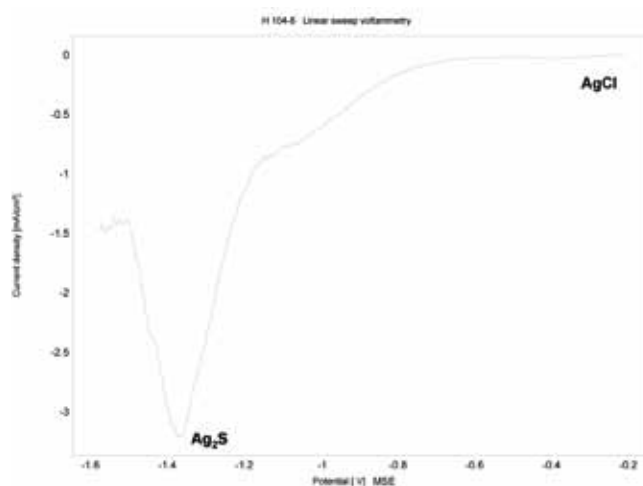
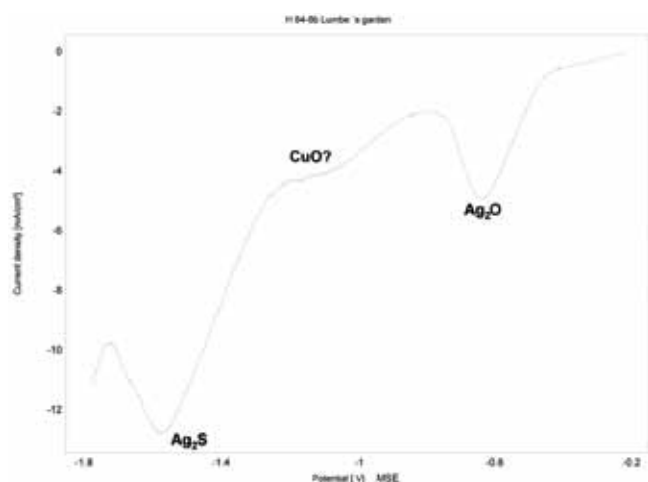


Fig. 4 Polarization plot recorded on a temple-ring with a lower content of silver and higher content of gold, group 2. (0.1 M  $\text{NaNO}_3$ , scan rate 10mV/s). The plot reveals presence of silver chlorides and silver sulphides

One peak of reduction corresponding to the peak of silver chlorides starts at -0.3 V/MSE, followed by a peak of reduction of silver sulphides starting at -1.2 V/MSE with a maximum of intensity at -1.38 V/MSE.

**Group 3:** earring (Ag 97%, 2.5% Cu, Au 0.3%, Pb 0.2%) (Fig.5).

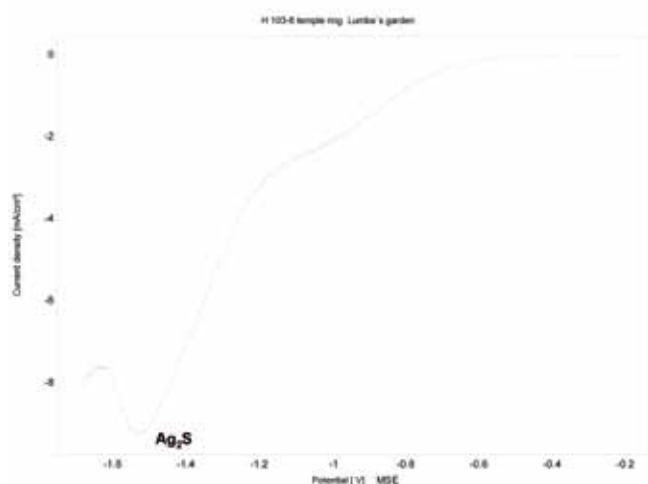


**Fig. 5** Polarization plots recorded on earring, group 3 (0.1 M  $\text{NaNO}_3$ , scan rate 10mV/s). The plot reveals presence of silver oxides ( $\text{Ag}_2\text{O}$ ), possibly also copper oxides ( $\text{CuO}$ ) and silver sulphides ( $\text{Ag}_2\text{S}$ )

A peak of reduction is starting at -0,55V with a max of intensity at -0.65 V/MSE. This peak can be identified as a peak of reduction of silver oxides.

Another peak seems to start a -0,8V/MSE and could be identified as a peak of reduction of possibly copper oxides. This peak is followed by another one starting at -1.2V/MSE with a maximum of intensity at -1.6V/MSE, corresponding to the peak of reduction of silver sulphides. Hydrogen evolution starts at -1.75 V/ MSE.

**Group 4:** temple ring with higher concentration of copper, group 4 (Ag 93.9%, Cu 4.5%, Au 1.2, Pb 0.4%) (Fig.6).



**Fig. 6** Polarization plot recorded on temple-ring with higher concentration of copper, group 4 (0.1 M,  $\text{NaNO}_3$ , scan rate 10mV/s). The plot reveals presence of silver sulphides

The peak of reduction of silver sulphides is present. It starts at -1.2V/ MSE with a maximum peak of intensity at -1.55 V/MSE.

Obtained polarization curves seem to show that the element of the tarnished layer is varying according to the objects. Silver chlorides are present as well as silver sulphides, possibly also copper and silver oxides. The maximum of intensity reached by the peaks of reduction of silver sulphides is occurring at -1,4 V up to -1,55 V/MSE.

As Storme and Urban [2011] have noted, the presence of copper corrosion products is not linked necessarily to the percentage of copper in the alloy but also to the type of corrosion process. It also depends on the way artefacts were manufactured (e.g. use of copper in the solder). As regards to obtained polarizations plots, we opted for an imposed potential of -1.6 V/MSE. This value includes peak of silver sulphides reductions at its maximal intensity and ensures safe object treatment avoiding evolution of elemental hydrogen at the same time.

## POTENTIOSTATIC REDUCTION

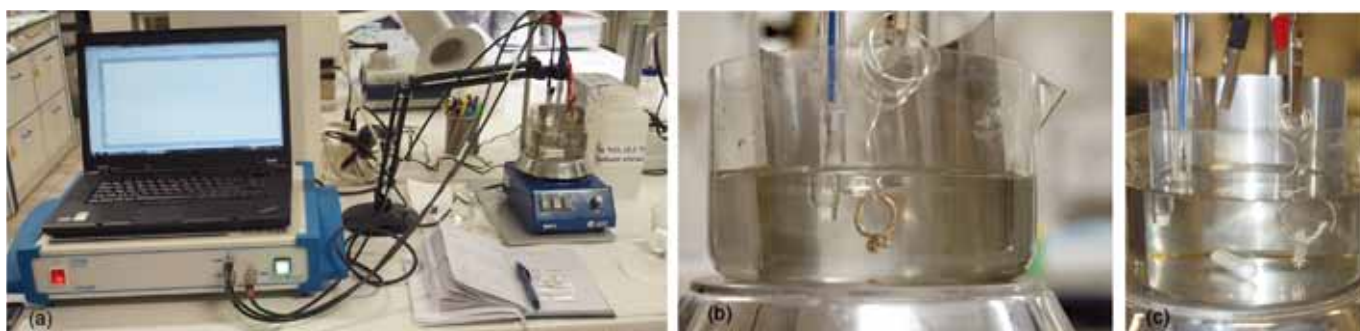
Once the potential of treatment was defined, artefacts were prepared to be cleaned by electrolytic reduction.

First of all, the artefacts were unvarnished, adhesives eliminated and the objects were degreased.

A three-electrode cell connected to a potentiostat (VoltaLab®, PST006 Education, Radiometer analytical) was set (Fig.7). The object placed as the working electrode, a stainless steel plate as the counter electrode, and a mercury sulphate electrode (MSE) (XR200, Radiometer analytical) as the reference electrode. The contact with the artefacts was provided with a wire of pure silver. Sodium nitrate at 0.1 M concentration was used as electrolyte. The solution was stirred during reduction to avoid redeposition of corrosion products.

The constant potential, corresponding to the maximum of intensity of peaks of reduction of sulphides of silver ( $\text{Ag}_2\text{S}$ ) as observed in the polarisation curves obtained above was set to -1,6 V (MSE) and the reduction of the tarnish layer was monitored by chronoamperometry. After reduction, the objects were taken out from the electrolyte, and the cell was disconnected. The artefacts were thoroughly rinsed under warm running water and gently brushed to remove newly reduced metal present on the surface as finely divided powder state. In most cases this approach appeared to be sufficient, but in some cases, the surface was dull and porous as it may happen after electrochemical cleaning [Costa, 2002, p. 93]. In that case, a gentle rubbing of the surface was performed using  $\text{CaCO}_3$  powder applied with swabs of cotton and ethanol. This helped to remove remaining reduced corrosion products and provided a soft burnishing of the surface which was heavily etched by previous alkaline cyanides cleaning.

Rinsing with tap water and distilled water followed, then the artefacts were immersed in ethanol and dried with an air blower. The objects were finally varnished twice in a 10% w/v acrylic resin solution in acetone, packed in polyethylene sealed bags, and placed in a hermetic box containing silica gel and sulphur absorbing material.



**Fig. 7** The three-electrode cell connected to the potentiostat (a); the three-electrode cell showing the temple-ring working electrode, the reference mercury sulphate electrode (MSE) and the stainless sheet counter electrode in the electrolyte (b); earring during treatment (c)

## STATE OF CONSERVATION AFTER TREATMENT

The tarnish layer which was covering the artefacts was removed successfully from all artefacts. SEM/EDS analyses after treatment have shown that no corrosion product was remaining on the surface (Fig. 8). Nevertheless, residues of abrasive ( $\text{CaCO}_3$ ) were detected by SEM/EDS analyses. It means that removal of abrasive is very difficult to achieve in particular if the surface is porous.



Fig. 8 Examples of artefacts after potentiostatic reduction

## STORAGE

Use of neutral storage material, control of environment (relative humidity) and proper handling are fundamental to avoid formation of further tarnish layer on the treated objects.

Wood, plywood, chipboards, wood paint coating, plaster, cardboard, textile, wood flooring must be avoided [Beldjoudi – Lacoudre – Dugot, 1999, p. 28]. Objects must be stored in neutral materials in hermetic boxes or cases containing silica gel, sulphur absorbing material [Lacoudre – Beldjoudi – Dugot, 1998, p. 268] and always handled with clean cotton gloves.

## CONCLUSION

Potentiostatic reduction has successfully removed the tarnish layer on all selected artefacts. This method appeared to be a good and quick alternative method to identify and remove superficial silver and copper corrosion products forming the tarnish layer on archaeological silver artefacts having a well preserved metallic structure. It appeared to be particularly well adapted to objects that underwent invasive chemical treatments in the past and which should not lose further metallic substrate, as well as to fragile objects which could be damaged by mechanical treatment. Finally, it is well adapted to objects presenting rich granulation decoration and recesses with difficult access to the tarnish layer.

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## REFERENCES

- BELDJOUBI, T. – LACOUDRE, N. – ESPIE, L. – DUGOT, J.: Etude prédictive de la sulfuration d'objets métalliques argentés. In: *la Lettre de l'OCIM*, n°66, 1999, pp. 25–30.
- COSTA, V.: The deterioration of silver alloys and some aspects of their conservation. In: *Reviews in conservation*. Number 2, 2001, pp. 19–35.
- COSTA, V.: Electrochemistry as a conservation tool: an overview. In: J. H. Townsend, K. Eremin and A. Adriens (eds), *Conservation Science 2002*. London: Archetype, pp. 88–95.
- COSTA, V.: *Museum's air quality in tropical climate: evaluation by using metallic coupons*. IAQ, Norwich, [http://iaq.dk/iap/iaq2003/2003\\_13.htm](http://iaq.dk/iap/iaq2003/2003_13.htm)
- COSTA, V. – DUBUS, M.: Impact of the environmental conditions on the conservation of metal artefacts: an evaluation using electrochemical techniques. In: *Museum Microclimates*, Padfield, T. (Ed.), The National Museum of Denmark, 2007, pp. 63–65.
- ČÁP, P. – MACHÁČEK, J. – ŠPAČEK, J.: *Tajemství výroby velkomoravského šperku, Archeologický experiment*. Praha: KLP, 2011.
- ESPIE, L. – LACOUDRE, N. – BELDJOUBI, T. – DUGOT, J.: L'électrochimie au service du patrimoine musical. In: *Techné*, vol. 12, 2000, pp. 19–27.
- LACOUDRE, N. – BELDJOUBI, T. – DUGOT, J.: Influence des conditions d'exposition et de protection des surfaces sur l'altération de plaquettes en laiton argenté au Musée de la Musique à Paris. In: *Metal 95*, Ed. William Mourey and Luc Robbiola, London: James & James, 1998, pp. 265–270. Electrochemical study of small brass plates exposed to different museum environments with and without the application of a corrosion inhibitor. (KL)
- OTTENWELTER, E. – HOSEK, J. – DĚD, J. – ŠTEFAN, I.: Manufacturing processes of S-shaped temple rings from Vrbno, Central Bohemia. In: *Archeologické rozhledy*, LXIV, 2012, sešit 3, pp. 525–533.
- STORME, P. – URBAN, F.: Elektrolytische reinigingstechnieken voor metalen, een onderzoeksproject uitgevoerd aan de Artesis Hogeschool Antwerpen, Opleiding Conservatie / Restauratie van Metalen. In: *Bulletin BRK-APROA*, Editie december 2011.
- SELWYN, L.: *Metal and Corrosion: A handbook for the Conservation Professional*. Ottawa: Conservation Institute, 2004.
- UNTRACHT, O.: *Jewelry, concept and technology*. London: Robert Hale, 1985.