

TWO CENTURIES OF CONSERVATION TREATMENTS ON ROMAN BRONZE STATUETTES FROM THE HUNGARIAN NATIONAL MUSEUM. HOW DO THEY AFFECT SURFACE ANALYSES?

A MAGYAR NEMZETI MÚZEUM RÓMAI BRONZSZOBRAINAK
KONZERVÁLÁSA AZ ELMÚLT KÉT ÉVSZÁZADBAN.
HOGYAN BEFOLYÁSOLJÁK A FELÜLETI VIZSGÁLATOKAT?*

GIUMLIA-MAIR, Alessandra¹  & BARTUS, Dávid² 

¹AGM Archeoanalisi, Merano, Italy

²ELTE Eötvös Loránd University, Institute of Archaeological Sciences, Budapest, Hungary

E-mail: giumlia@yahoo.it

Abstract

As a part of a larger project on Roman statuettes in Hungary we have also investigated the “restorations” and “improvements”, carried out over the past centuries on most of the earlier pieces we have analysed. The statuettes were acquired from excavations, donated by private collectors or possibly bought from other countries and underwent various treatments.

An artificial patina, in the form of a black lacquer, was applied to most of the figurines. Our examination showed that it is possible to distinguish the ones employed in the 19th century – or even earlier – from the reddish-brown ones employed in the early 20th century. Interestingly, these treatments show notable similarities to the artificial patinations applied to Roman objects recovered in the same periods discovered at Pompeii and elsewhere in the area. Interventions with electrolysis can also interfere with surface analysis of older museum pieces. Another noteworthy aspect is the range of “improvements”, additions and “repairs” performed on some of the statuettes. In several cases, missing limbs, body parts or attributes were reconstructed by the “restorers” who tried to “improve” the objects by coating them with some kind of artificial patina to homogenize their appearance. This is a relatively common phenomenon that can be observed in most of the collections acquired by larger museums in different ways in the 18th and the 19th centuries.

The primary aim of this paper is to highlight the impact that older “restorations” of various kind can have on surface analyses of the artifacts. This paper presents some case studies from the Hungarian National Museum in Budapest and compares them to artefacts from other Roman sites in Italy.

Kivonat

A Magyarországról előkerült római kori bronzszobrokkal foglalkozó OTKA-projekt kapcsán azokat a „restaurálásokat” és „javításokat” is vizsgáltuk, amelyeket az elmúlt évszázadokban végeztek az általunk elemzett darabok nagy részén. Ezek a tárgyak ásatásokból származnak, magánszemélyek adományai, esetenként más országokból vásárolták őket, és különböző felszíni kezeléseken estek át.

A legtöbb tárgyon mesterséges patinát alkalmaztak fekete lakkréteg formájában, és az elemzések kimutatták, hogy a 19. században – vagy még korábban – alkalmazott eljárásokat meg lehet különböztetni a 20. század elején alkalmazott vörösesbarna patinától. Érdekes eredmény, hogy ezek hasonlóságot mutatnak a Pompeiiből előkerült római kori tárgyakon ugyanebben az időszakban alkalmazott mesterséges patinákkal. Az elektrolízises beavatkozások szintén gátolják a régebbi múzeumi darabok felszíni vizsgálatait. Fontos vizsgálati téma az egyes szobrokon végzett „javítások” és kiegészítések technikája. Egyes szobroknak például hiányoztak a végtagjai, egyéb testrészei vagy attribútumai, így a hiányzó részek hozzáadásával és valamilyen mesterséges patinával való bevonással igyekeztek javítani a megjelenésükön. Ez a gyakori jelenség a legtöbb, nagyobb múzeumhoz tartozó, régebbi, a 18–19. században szerzett gyűjtemény leletanyagában megfigyelhető.

* How to cite this paper: GIUMLIA-MAIR, A. & BARTUS, D., (2025): Two centuries of conservation treatments on Roman statuettes, *Archeometriai Műhely* XXII/3 249–264.
doi: [10.55023/issn.1786-271X.2025-019](https://doi.org/10.55023/issn.1786-271X.2025-019)

A jelen tanulmány fő célja a különböző típusú régi “restaurálások” felszíni vizsgálatokra gyakorolt hatásának bemutatása a Magyar Nemzeti Múzeumból származó esettanulmányok és olaszországi lelőhelyekről származó párhuzamok bemutatásával.

KEYWORDS: ROMAN BRONZE STATUETTES; HUNGARIAN NATIONAL MUSEUM; XRF; SEM-EDS; ICP-OES; ARTIFICIAL PATINA

KULCSSZAVAK: RÓMAI KORI BRONZSZOBROK; MAGYAR NEMZETI MÚZEUM; XRF; SEM-EDS; ICP-OES; MESTERSÉGES PATINA

Introduction

Archaeological bronze artifacts from historical collections – such as the Roman statuettes in the collections of the Hungarian National Museum (HNM) in Budapest, which represent the focus of this paper – but also objects in many more museums around the world – underwent cleaning and restoration in the past, sometimes multiple times. Regrettably, in most cases, detailed documentation on the earlier restorations, reconstructions or additions is lacking. The absence of records poses significant challenges for today’s scholars analysing the artifacts, as well as for conservation specialists, who need to update the conservation treatments. Not many studies have been carried out on how previous treatments might influence surface analyses, such as X-ray fluorescence (henceforth XRF), the method employed in this research or Scanning Electron Microscopy with Energy Dispersive Spectrometry (henceforth SEM-EDS).

Understanding past restoration procedures is crucial to avoid inaccuracies or misinterpretations, especially in cases when artifacts have been treated with acids, subjected to electrolysis and then covered with various kinds of artificial patinae produced by applying a coating or by using chemicals. In most cases, the lack of archive documentation represents a problem, and a scientific investigation is required to identify historical conservation treatments and evaluate the current condition of the objects. Studying the techniques and materials employed in past interventions can help researchers determine the appropriate approach to the study of these pieces. This paper does not aim to present a history of conservation – which would be out of place in this context and beyond the scope of this study - but rather to explore how past treatments, such as the coatings, artificial patination with acids and cleaning through acids and electrolysis may affect surface analyses. The paper is based on data collected from a small group of statuettes analysed in 2023 in the National Museum Budapest with comparisons from the National Archaeological Museum in Naples. Additional interesting aspects include reconstructions, additions and repairs observed on the statuettes.

Analytical methods

All Roman copper-based statuettes from the collections of the Hungarian National Museum studied for this project (250 pieces in total) were first autoptically examined with various magnification devices and viewed under a microscope to determine the conservation condition. The primary objective of this examination was to identify the most suitable area for performing the measurements. As a non-destructive method was required, we selected X-ray fluorescence analysis. XRF is a well-established and widely used method in archaeometry (Lutz et al. 1996; Helmig et al. 1989; Longoni et al. 1998; Mendoza Cuevas & Perez Gravie 2011; Soles & Giunlia-Mair 2018; Giunlia-Mair et al. 2015). The equipment employed for the analysis in the museum is a transportable X-ray fluorescence analyser consisting of various parts that can be mounted wherever necessary, even on excavations. It has been specifically developed for the analysis of cultural heritage objects by the company Assing in collaboration with experts of the Centro Nazionale di Ricerca (CNR) in Rome. The system comprises a modular setup suitable for both laboratory use and on-site applications. The head of the system integrates an X-ray source and a Si(Li) detector (~8 µm) with a beryllium window, along with a Class2 laser pointer (695 nm) for precise targeting of the measurement area (collimator, diam. 1 to 4 mm). The head is mounted on an adjustable tripod and emits acoustic feedback to ensure the correct focal distance (within +/- 0.1 mm). Additional built-in devices monitor position and stability during measurements. The spectrometer operates at a max. voltage of 50 kV and a max. current of 0.35 mA. Its energy resolution is <145–160 eV at Mn K α (5.9 keV). The system is supported by a transformer, a voltage stabilizer and a laptop computer running dedicated software developed by Assing for the analysis of ancient metals (Assing 2020, 15-16). The measurements were conducted at a fixed angle and controlled distance, exclusively on clean areas, corrosion-free and mostly free of patina. Exceptions were made for a few measurements on flat areas with a thin, compact and stable noble patina, which has been demonstrated to have minimal impact on analytical results, (Lutz et al. 1996; Helmig et al.

1989; Longoni et al. 1998; Robotti et al. 2018; Giumlia-Mair 2022a, 89-90). Measurements on rough or porous patina were avoided. A minimum of three XRF measurements were carried out on each object, with additional readings performed in the case of ambiguous results, due for instance to complex geometries of items with an awkward shape or to possible vibrations during acquisitions. Elemental concentrations under 0.2 weight% have been considered as traces. The quoted detection limits (in ppm) were as follows: (in ppm) Pb 5–20; Sn 10–30; Fe 10–30; Co 10–30; Ni 10–30; As 20–50; Sb 15–40; Ag 5–15; Zn 10–30; Mn 15–40. For copper, results are expressed in weight percentage with a typical accuracy in the range of +/- 0.1–0.3%; The calculated precision is approximately +/- 1% for copper, +/- 2% for elements present in concentrations above 2 weight% and gradually and proportionally decreases to +/- 30% for elements near the detection threshold. To enhance data quality, relatively long acquisition times (200–300 seconds) were used.

Prior to each measurement session and whenever the equipment was switched off, standards with known composition were run to ensure reliable results. The standards, produced by AGM-Archeoanalisi, consist of polished specimens with compositions as similar as possible to ancient copper-based and silver-based alloys. They were analysed by ICP-OES after casting to obtain a precise composition. In this way drift, matrix and interference effects could be precisely monitored and taken into consideration when calculating the results with the dedicated software (see e.g. Soles & Giumlia-Mair 2018; Giumlia-Mair et al. 2023, 14).

Table 1.: X-ray fluorescence results (in weight%) obtained from the measurements on the five statuettes discussed in the present paper. Results from measurements on the coating are only expressed qualitatively with +++; ++; and +.

1. táblázat: A jelen tanulmányban tárgyalt öt szobron végzett XRF-mérések eredményei, tömeg%-ban megadva. A bevonaton végzett mérések eredményei csak minőségileg jelezve (+++; ++; +).

Nr.	Object	Inv.nr.	Part	Cu	Sn	Pb	As	Sb	Fe	Ni	Ag	Zn	Mn
52	Lar	54.18.17	body	80	10.1	7.9			1.9				
52			coating	+++	++	++			++	+			
19	Fortuna	100.1895.38	body	78	7.8	10.2		tr.	0.4			3.7	
19			coating	+++	++	++			++	+			+
252	Venus	129.1895	body	89	8.4	2.5			0.2				
42	Bacchus	3.1944	head	75	6.7	18			0.2				
43			repair	86	6.4	7.6			tr.				
44			plate	75	7.5	16			1.5				
03	Minerva	105.1895.4	body	86	8.9	4.3			0.7				
04			arm fracture	73	7.4	3.4			0.3			16	
05			left arm	68	1.7	3.2			0.2			27	
06			shield	tr.					tr.				
07			shield	65	2	3.8			0.2			29	

For this paper we selected 5 representative pieces, as examples of different conservation treatments conducted in past centuries. The results of the XRF analyses are reported in **Table 1**.

Results

In the following text the term “patina” refers specifically to a natural patina, while “artificial patina” is employed as general term to describe either coatings made from various materials imitating a natural patina, or artificially induced corrosion layers produced with acidic copper salts, intended to imitate a natural patina. The specific methods and materials employed for individual items are discussed in detail for each piece.

As XRF is not suitable for analysing organic materials – such as the coatings on the statuettes – but can determine inorganic pigments mixed with the material of the coatings, the results must be regarded as semiquantitative. For this reason, the data from the coatings are expressed with “+++” for high concentrations, “++”, for medium levels, and “+” for low levels (see **Table 1**).

A very evident and recurring treatment on many of the objects is the application of an artificial patina, in the form of a thick, black lacquer. An example is a Lar statuette (HNM Inv. no. 54.18.17; **Fig. 1a**) cast in common leaded bronze, containing approx. 10 weight% Sn and 7.9 weight% Pb, completely coated with a black and thick lacquer. The XRF measurements revealed elevated levels of iron and calcium in the coating, while these elements were lower or absent on areas where the black lacquer was worn.

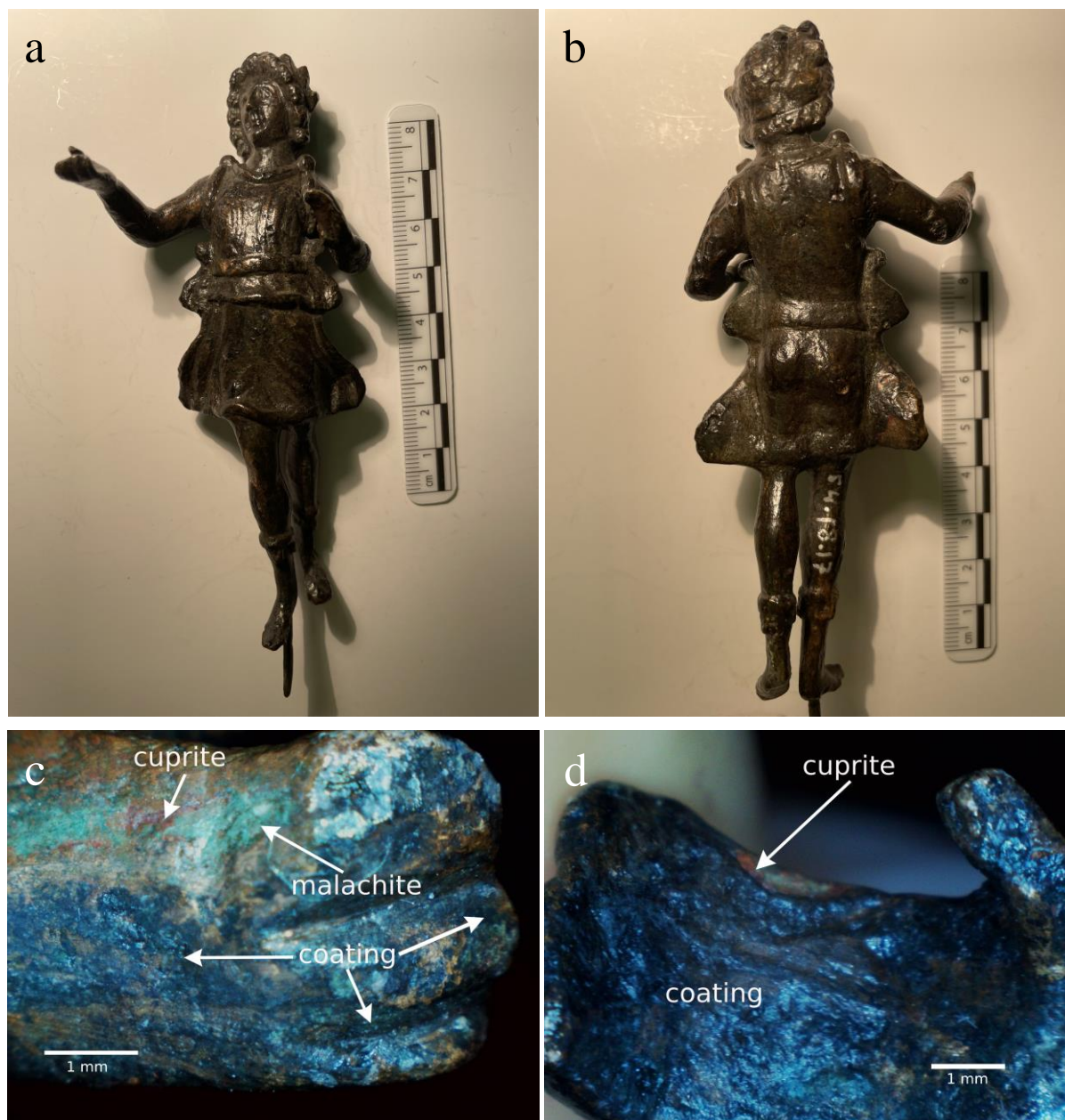


Fig. 1.: Lar statuette (HNM Inv. no. 54.18.17), made of leaded bronze (80 weight% Cu, 10 weight% Sn, 7.9 weight% Pb). **a** – Front: The statuette is covered by a thick black lacquer. **b** – Back: The figurine was produced by taking a cast from a naked statuette and adding the flowing Lar garment at the front, without bothering to add it to the back. **c** – Micrograph of left-hand detail showing that the original patina was removed down to the metal. Some remains consisting of a layer of red cuprite under green malachite are still visible at the top, while the black lacquer partly covers the rest. 50 X magnification. **d** – Detail of right hand, covered by a thickly applied black lacquer. On the side some cuprite and possibly malachite are still visible. 50 X magnification. (Photos A. Giunlia-Mair)

1. ábra: Lar szobor (MNM Ltsz. 54.18.17), ólmozott bronz (80 tömeg% Cu, 10 tömeg% Sn, 7.9 tömeg% Pb). **a** – Előnézet: A szobor vastag fekete lakkréteggel van bevonva. **b** – Hátsó nézet. A szobrot egy meztelen szobor leformázásával készítették, az elülső felén elkészítették Lar ruházatát, a hátsó rész kialakításával nem foglalkoztak. **c** – Mikroszkópfelvétel a bal kéz részletéről. Az eredeti patina a fémig eltávolításra került. A felső részen még láthatóak egy zöld malachit alatti vörös kupritréteg maradványai, a többi részen a fekete lakkréteg borítja. 50-szeres nagyítás. **d** – A jobb kéz részlete, vastagon bevonva fekete lakkréteggel. Az oldalán egy kevés kuprit és talán malachit még látható. 50-szeres nagyítás. (Fotók: A. Giunlia-Mair)

This Lar statuette is rather interesting, because the figurine was produced by taking a cast from a naked male statuette, possibly a Mercury or Apollon, as can be clearly seen on the shape at its back side (**Fig. 1b**). The arms were repositioned to hold a patera and a cornucopia. Finally, the typical flowing garment of a Lar was added on the front, while the back remained unchanged. This kind of black coating needs to be discussed in more detail.

18th–19th century: black coatings

Items covered by an artificial patina, consisting of a black, thickly applied lacquer (see **Fig. 1c-d**), are found in the older collections of many European museums (see e.g. Peltz 2021, 128–132). A good example from a different context is a lamp-tintinnabulum element representing an ithyphallic dwarf statuette from Pompeii (1st century AD), an old find, now in the National Museum in Naples (inv. no. MANN 27873; Pfisterer-Haas, 2023, 317–318, fig. 42; Kat. 94), like the Lar, covered by the same kind of black patina. The analyses on both objects revealed comparable results: enhanced calcium and iron levels on the coating and only traces of these elements on blank metal (Giumlia-Mair 2022a).

Anne-Claude Philippe de Tubières, in general just known as count of Caylus (1692–1765) a prominent antiquarian and collector, member of the Académie des Inscriptions et Belles Lettres and of many more cultural institutions, believed that Roman bronzes were black, because of a passage in the Natural History of Plinius the older, who mentions statues painted with bitumen (Pliny, Nat. Hist., XXXIV, 15). Caylus was a well-known and appreciated scholar, he and his publications were influential among people who at the time collected and studied ancient objects. Caylus repeatedly claimed that his Roman pieces found at Chalon-sur-Saône bore originally a black coating (Caylus 1752–1755). However, there is no documented archaeological evidence of bronzes with black coating, and no lacquer would survive a prolonged burial.

Similarly, the 19th century British collector Richard Payne-Knight had artificial black patinae applied to the objects in his collection. His blackened pieces are still now easily recognizable in the showcases of the British Museum (Craddock & Giumlia-Mair 1993, 31). This idea influenced many museums, dealers and collectors throughout Europe, and in the 19th century many pieces belonging to European collections were painted black.

An illustrative case is a lamp from Pompeii, decorated with a 21.6 cm high statuette of a dancer, excavated in the 18th or 19th century, now in the National Archaeological Museum in Naples (inv. no. MANN 72254, **Fig. 2**). Analyzed by one of the authors in 2019 (Giumlia-Mair 2022a), this piece underwent an analysis by XRF and was sampled

with a drill, to be analysed by ICP-OES. All parts of the lamp, lamp's body, reflector, statuette, handle, chains and lock have been analysed, but here we only give the most important data: the lamp consists of an alloy with 75 weight% Cu, 11 weight% Sn and 17 weight% Pb (ICP-OES). The dancer boy statuette contains 74 weight% Cu; 7.4 weight% Sn and 21 weight% Pb. The ICP-OES analyses were done at the Ludwig-Maximilian University in Munich at the Department for Chemistry, Section for Central Analytics by J. Obel. The equipment was a sequential ICP-OES, so, the reason why the results do not sum up to 100% are small instrumental errors due to the fact that the elements were analysed one by one. The XRF analysis performed on the same parts of the objects gave the following results: for the lamp 74 weight% Cu; 10 weight% Sn; 15 weight% Pb. For the statuette the results were: 72 weight% Cu; 7.2 weight% Sn; 20 weight% Pb. The XRF analyses determined results similar to those of ICP-OES, but also high calcium, iron and nickel content, clearly coming from the material of the black coating applied in modern times.



Fig. 2.: Dancer statuette, decoration on lamp from Pompeii, now in the National Archaeological Museum in Naples (Inv. no. MANN 72254). The black coating applied in modern times contains iron and nickel. (Photo A. Giumlia-Mair)

2. ábra: Táncos szobra Pompeiiből, Nápolyi Régészeti Múzeum (Inv. no. MANN 72254). A modern fekete bevonat vasat és nikkelt tartalmaz. (Fotó: A. Giumlia-Mair)

The large lamp's reflector with double volutes and a central palmette was originally tinned (Giumlia-Mair 2022a, 98–99, Fig. 11.11).

The situation is slightly different with some finds from the Vesuvian area, which were blackened by the eruption. Items from Herculaneum in particular appear blackened due to thermal alteration and exposure to sulphur vapours, while some bronzes from Pompeii and other sites around the Vesuvius did not show any such discoloration. For instance, a lamp-tintinnabulum in shape of an ithyphallic dwarf (inv. no. MANN 27870; Pfisterer-Haas 2022, 318–320, Kat. 96, 420, Fig. 42.7) was already black when it was recovered from the soil. It was subsequently cleaned with part of the corrosion removed, before the usual black lacquer was applied on the surface and then placed on a base of some lost statuette (Fig. 3). We could analyse a small sample of the coating by SEM-EDX, but it only confirmed the presence of calcium, iron and nickel in the artificial patina. Apparently, it consists of an organic basis of some kind, possibly wax or some natural resins, mixed with a black pigment containing iron and nickel salts (Giumlia-Mair 2022a). Similar mixtures have been employed on many finds in large museums, including the National Museum in Budapest, in the 18th–19th centuries and possibly even later.

A report in the archives of the Römisch-Germanisches Zentralmuseum at Mainz without a date, but certainly written before 1887, describes this procedure: «The bronze is (mechanically) cleaned like iron, washed, heated and coated with pure wax. When it penetrates (the metal) and dries, the object is brushed with a brush made of goat hair until a matte sheen, similar to that of a patina, is created. If later some mushroom-shaped verdigris growth appears, it has to be cut away with a sharp instrument and the exposed spot can be dabbed with a «gum solution» (see Peltz 2021, 82).

It is plausible that in Budapest and Naples similar procedures were adopted.

In the 18th–19th century additional materials, such as paraffin, linseed oil, nitrocellulose (cellulose nitrate) and celluloid varnish, were applied on bronzes, both as protection and to homogenize the colour of the surface. Quite often, before the application of these materials, the objects were also exposed to high temperatures or treated with acids to eliminate the corrosion layers, quite often with detrimental results.

19th–20th century treatments

In the 19th–20th centuries and in some cases until today, collodion, a solution of nitrocellulose in ether and alcohol, was employed to consolidate corroded bronzes. Nitrocellulose (also known as cellulose nitrate) is a nitrated polysaccharide

derived from cellulose, widely utilized in materials science for its film-forming properties. Although the terms “cellulose nitrate” and “nitrocellulose” are used interchangeably in the literature, this paper will refer to the material as “nitrocellulose” for consistency, in line with the prevailing scientific terminology. This material is initially colourless, can be coloured with pigments but it discolours over time. It cannot be identified with XRF, but the pigments added introduce elemental signals that will be determined, and this interferes with the analysis results of the underlying metal. This material was widely used, and it is important to mention it.

A further material that was employed in this period is zaponlack, a commercial solvent-based varnish made with nitrocellulose, the only one available in the early 20th century in Hungary.



Fig. 3.: Statuette of an ithyphallic dwarf, originally from a hanging tintinnabulum-lamp from Pompeii, as indicated by eyelets on the phallus from which bells used to hang. The figurine was mounted on the base of a lost statuette after it was found. Its surface was blackened by sulfur vapors during the eruption of the Vesuvius and then covered by a black coating containing iron and nickel salts. (Photo A. Giumlia-Mair)

3. ábra: Ithyphallikus törpe szobra, eredetileg egy függesztett tintinnabulum lámpáról Pompeiből, amit a faloszon lévő akasztók is jeleznek. A szobrot a megtalálás után egy már elveszett szobor bázisára erősítették. A felszínét a Vezúv kitörésekor kén-gáz feketítette be, majd vas és nikkelsókat tartalmazó fekete bevonattal vonták be. (Fotó: A. Giumlia-Mair)

It was also employed for the consolidation of corroded bronzes (Maier & Peltz 2013). This material has a high surface resistance and can be removed with amylacetate, ethanol, acetone or ethylacetate. Nowadays it is still, in some cases, used as a protection for metals and gilding on metals. Like collodion, it cannot be identified with XRF, but it can be also coloured with pigments to achieve the desired nuance for the artificial patina, again potentially interfering with the analyses. As already noted, the taste and the ideas on the patination colour of copper-based items evolved and changed with time.

Reduction by electrolysis

In the 20th century, with the beginning of “scientific” attempts at restoration and conservation, practices changed. In 1898 Rathgen, the chemist at the Museum in Berlin, published his «Handbuch» and described the “new process of conservation by reduction”: electrolysis (Fig. 4.), one of the most common methods employed in restoration in this period (Rathgen 1898; 1905, 125–144). From then on in all museums in Europe and around the world, copper-based items were electrolytically cleaned, regrettably quite often with disastrous outcomes and only sometimes with “less-than-optimal” results.

The Isis Fortuna statuette from Brigetio (Fig. 5a), belonging to the collection of the Hungarian National Museum (inv. no. 105.1895.38.), may also have undergone electrolytic cleaning and repatination. Alternatively, an older, even worse and

harsher method might have been employed: a “cleaning” treatment with strong acids, such as sulphuric (H₂SO₄), hydrochloric (HCl) or nitric acid (HNO₃). This method is aggressive, difficult to control and can dissolve both, corrosion products and underlying metal, which is destructive and irreversible. Wherever acids were used in the past, they can significantly alter surface chemistry, removing or redistributing corrosion stratigraphy, and biasing surface analysis results, like those from XRF. As no documentation exists, electrolysis was widespread as cleaning method and was indeed in use in the National Museum both hypotheses are plausible.

Microscopy on the Isis Fortuna shows cuprite covered by a dark artificial patina, making an electrolytic treatment more probable, because a treatment with acids would be less well controlled, and this piece still shows a cuprite layer. The detail of the face shows that the corrosion was removed by the treatment and left some voids and pitting. Some remains of the green patina are still recognisable on top of the red cuprite layer on the face and in the hair (Fig. 5b). In some places, for example on the folded garment at the belt, the wear exposed the core metal (yellow spots) and cuprite (red spots) under the black lacquer (Fig. 5c), applied on the surface after the treatment: The colour is not as black as on the previous examples but rather reddish-brown, indicating thus the use of different coatings, possibly just the same kind of base prepared with different pigments. The XRF analysis on the coating indicated again an enhanced presence of iron and nickel.

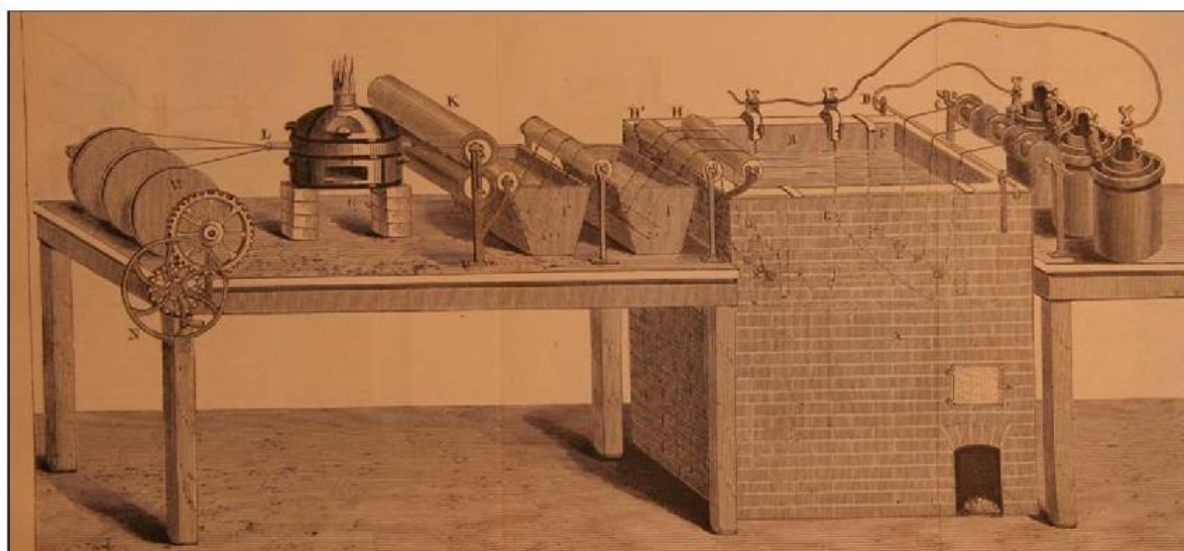


Fig. 4.: 19th century representation of the system for electrolysis and galvanoplastic. In 1924 Rathgen published his «Handbuch» describing the new process of «conservation by reduction». (Photo: A. Giumlia-Mair with permission of Museo Civico di Storia Naturale di Trieste, Italy)

4. ábra: Az elektrolízis és galvanoplasztika rendszerének 19. századi ábrázolása. 1924-ben Rathgen “Handbuch”-jában publikálta a “redukciós konzerválás” új módszerét. (A fotót A. Giumlia-Mair készítette a Museo Civico di Storia Naturale di Trieste engedélyével.)

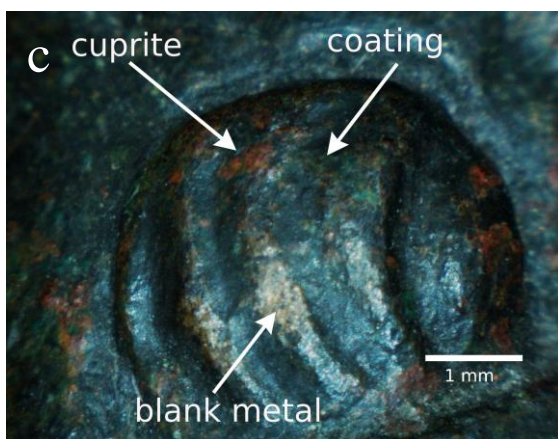
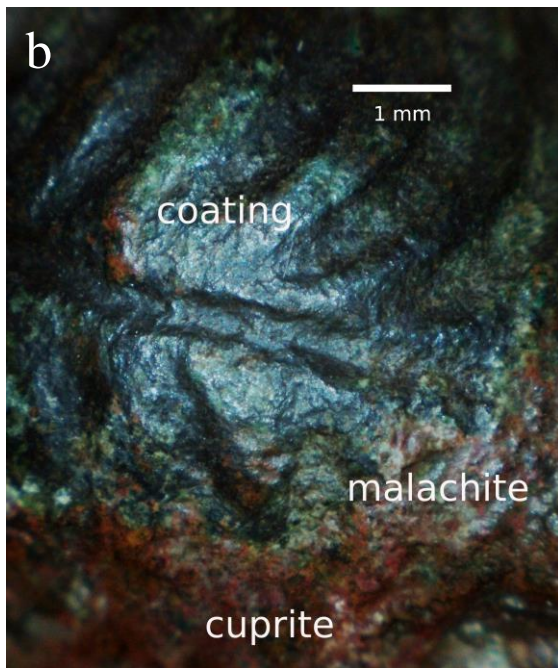


Fig. 5.: Isis Fortuna (HNM Inv. no. 100.1895.38). **a** – Presumably electrolytically cleaned or, less likely, treated with acids and then repatinated. **b** – Some remains of the green patina are still recognizable on the red cuprite layer in the hair at the top of the head and under the black lacquer. **c** – Detail of the folded garment at the belt. Microscopy shows some cuprite covered by a dark artificial layer. The light color is the blank metal. 50 X magnification. (Photo A. Giumlia-Mair)

5. ábra: Isis Fortuna (MNM Ltsz. 100.1895.38). **a** – Valószínűleg elektrolízissel tisztítva vagy, kisebb valószínűséggel savakkal kezelve és újrapatinázva.

b – A zöld patina maradványai még felfedezhetőek a vörös kupritrétegen a hajban a fej tetején és a fekete lakkréteg alatt.

c – A derékra csavart ruha részlete. A mikroszkópos vizsgálat fekete, mesterséges réteggel bevont kupritot mutatott ki. A világos szín a nyersfém. 50-szeres nagyítás. (Fotó: A. Giumlia-Mair)

Having analyzed around 250 pieces, we have been able to notice that pieces with older inventory numbers in the Hungarian National Museum seem to be predominantly covered with black lacquer, while those with later inventory numbers mostly show a reddish-brown coating. The analyses showed 7.8 weight% Sn; 10.2 weight% Pb; 3.7 weight% Zn. Both Sn and Pb concentrations were possibly higher in origin but disappeared because of selective corrosion of elements higher than copper in the activity series of metals, and the treatment for the removal of the corrosion layers.

It is important to note that the traces of Zn come most probably from the electrolytic cleaning process. The 3.7 weight% of zinc determined by the surface analysis, must be a residue left by the treatment rather than being an alloying element. As a piece of zinc was commonly employed as electrode in the electrolysis, most objects that have been electrolytically treated show zinc enrichment, sometimes up to 7–8 weight%, but only on the surface (Xu et al. 2017; Jansen et al. 2023, 21-23; for more insights into unwanted zinc deposition mechanisms see also Vijjaratnam et al. 2017; Popov et al. 1978). It is obviously important to be aware of this issue.

As demonstrated by many thousands of analyses of these items all over Europe, Roman statuettes generally show only very low zinc contents at trace level that usually can only be detected with precise destructive methods such as Atomic Absorption Spectrometry or Inductively Coupled Plasma Optical Emission Spectrometry, but not with XRF. As already shown early in the last century, by the analyses of Davies (1935, 60) and Caley (1964, 13) copper-zinc alloys circulated as precious and rare

materials in the 5th–4th centuries BC in Greece and presumably came from the area of Balya Maden in Anatolia (Caley 1964, 18-25; Craddock 1998, 3; Craddock & Eckstein 2003). This alloy, called oreichalkos (ὀρείχαλκος, copper of the mountains) in Greek, was highly valued (Homer, Hymn to Aphrodite, 6, 9; Hesiod, Shield of Heracles, 122). According to Strabo (Geographica, 13, 56), it was produced in Andeira (Balya Maden) by mixing with copper the rare metal “mock-silver” i.e. zinc, found as silvery droplets coming from the upper, cooler part of the local furnaces in which silver was reduced from mixed ores (galena, sphalerite and pyrite). The zinc present in the sphalerite evaporated during melting and condensed in the upper part of the furnace and, added to copper, was used only for jewellery and small, precious, decorative objects. Later, the copper-zinc alloy brass was produced by cementation process in a crucible and has a characteristic composition that permits to distinguish it from modern brasses (Bayley 1998, 9).

Brass, leaded brass and quaternary alloys were introduced in the Roman world in the 1st century BC (Craddock & Eckstein 2003; Istenič & Šmit 2007), apparently by metalworkers belonging to the Roman army, notably by Caesar’s legions, who had learnt how to use zinc ores and cementation in Anatolia and Gallia (Giumlia-Mair 2025). Analyses indicate that freshly produced brass was only employed for coins and military equipment, suggesting that it was a state monopoly. Ordinary people had instead coins melted and mixed with copper or bronze to obtain shiny and almost golden-coloured personal ornaments (Giumlia-Mair 2025, 359-363). However, with few exceptions from France or the Rhine area (and fakes and imitation figurines produced – especially, but not exclusively - in the 19th century), statuettes were mostly made of leaded bronze and did not contain zinc in significant amounts. The possibility that the presence of zinc in some figurine is due to the use of scrap metal containing fragments of small decorative objects, like fibulae, cannot be ruled out, however, analyses of Roman objects clearly illustrate that, especially in the 1st–2nd centuries AD, and also later, the metalworkers usually kept carefully separated from bronze or leaded bronze the damaged items containing zinc (brass or leaded brass), to reuse them for similar types of objects (see e.g. Craddock 1985; Picon et al. 1966; 1967; 1968; Antonacci Sanpaolo et al. 1992; 1993; Giumlia-Mair 1993; 1996; Riederer 2002a, 286; 2002b; Thomas 2002, 302).

A second example of a potentially electrolytically treated piece is a Venus statuette (HNM Inv. no. 129.1895, **Fig. 6a-b**). This item was evidently corroded, and the electrolysis or, alternatively, a chemical treatment by acids removed the patina quite completely. The removal of corrosion layers produced holes in the areas, more affected by corrosion, in particular the details of the face. Even the edges of the repair at the back, where the patch is lost are blurred and rounded (**Fig. 6b**). The shape of the hand is now angular, and the fingertips are partly missing. **Fig. 6c** shows the detail of the left eye. The eye socket is much larger than it was originally, all details of eyelids and eyeball are lost, with part of the nose missing. The same happened with lips and chin (**Fig. 6d**). Part of the green crusts in the eye sockets and the crater of the mouth might be residues of natural patina. The green artificial patina directly applied on blank metal instead was produced with some kind of acidic solution of copper salts, as its typical runny appearance and the lack of underlying cuprite suggest (see **Fig. 6e**). Of these solutions there are many recipes that cannot be detailed here because this discussion would transcend the scope of the paper (Buchner 1914; Hughes & Rowe 2009). The examination under the microscope showed that the treatment dissolved the tin-rich dendrites on the surface, leaving the more corrosion resistant phase alpha of the metallographic structure. This can be clearly seen from the dendrite ghosts visible e.g. on the buttock of the statuette (**Fig. 6e**). The rounded, smaller black dots are the places where the now missing lead globules were positioned in the metal, while the larger ones come from corrosion pitting. As it is well known, lead is not soluble in copper and builds small or larger globules (depending on the amount of lead present in the alloy) that are normally diffused in the metallographic structure, but can concentrate in thicker parts of the castings as happened in this statuette, or in peripheral parts. The segregation phenomenon illustrated by this statuette might possibly be due to inverse segregation (i.e. lead pushed to the surface, forced by shrinkage) or, if the mould was left laying during the cooling phase, it could be the result of gravity segregation (i.e. the lead would move to the bottom instead of being dispersed in the alloy). This also means that the elements tin and lead might be higher in the core metal of the statuette. The XRF measurement identified copper containing 8.4 weight% Sn and 2.5 weight% Pb. In particular, the lead seems rather low, thinking of the many typical voids seen by microscopy on the surface of the statuette.

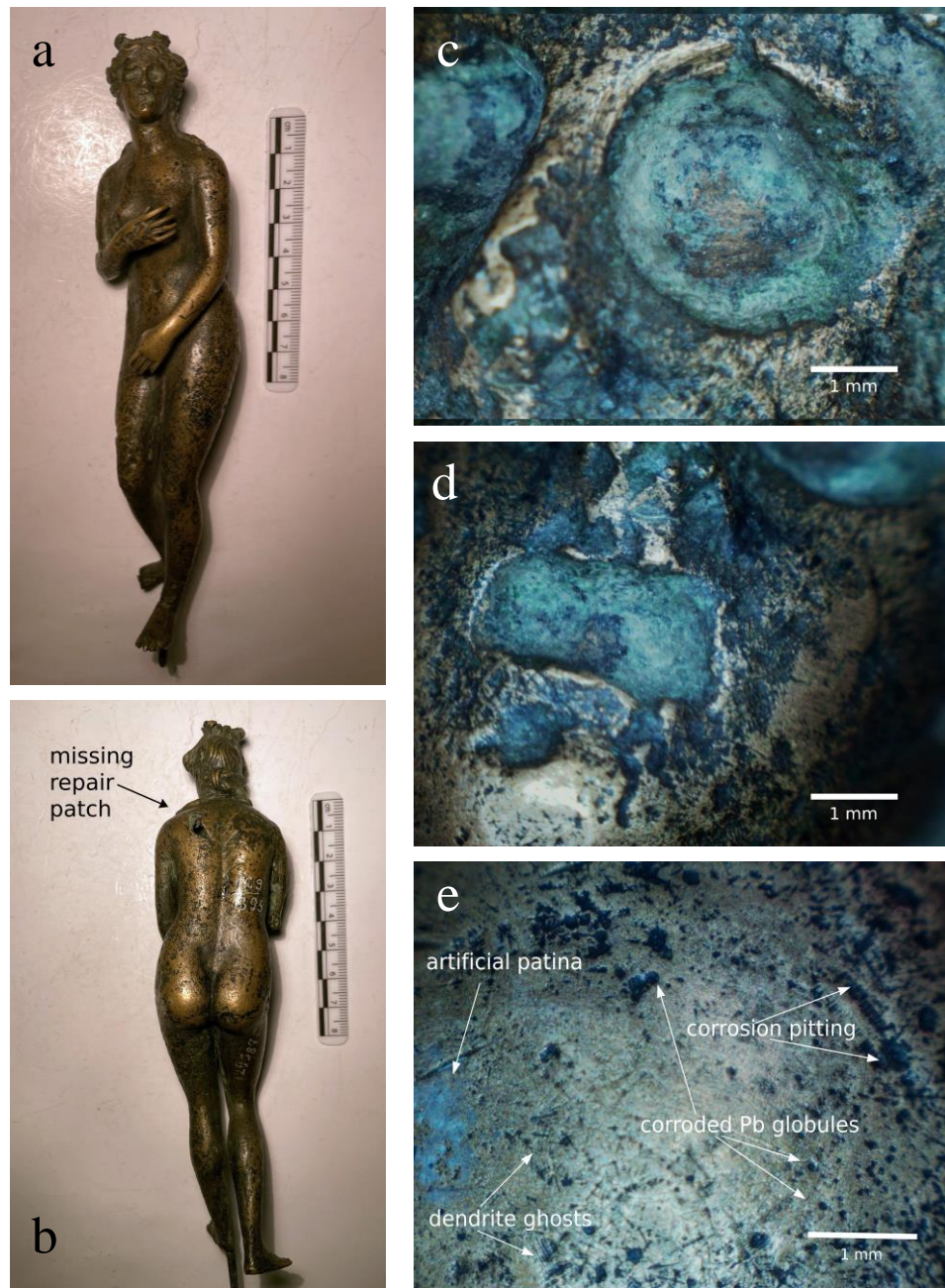


Fig. 6.: Venus (HNM Inv. no. 129.1895).

a – Front. The statuette was electrolytically stripped or treated with acids. **b** – Back side. On the right shoulder a repair patch was lost, and its contours are blurred by the treatment. **c** – Detail of eyes without any remains of lids and iris and eroded nose. The removal of corrosion by electrolysis or acids produced large holes and destroyed the facial features. X 50 magnification. **d** – Detail of eroded mouth and chin. The thicker green crusts in eye sockets and mouth are residues of the original patina, while the thinner green layers on blank metal without any underlying traces of cuprite (see fig. 6e) come from an attempt to artificial patination. X 50 magnification. **e** – The electrolytic treatment evidenced the shape of dendrites on the buttock. The smaller round holes were left by now missing lead globules, the larger craters come from corrosion pitting. On the left some green artificial patina was likely produced with an acidic solution of copper salts. X 50 magnification. (Photos A. Giunlia-Mair)

6. ábra: Venus (MNM Ltsz. 129.1895).

a – Előnézet. A szobor elektrolízissal tisztított vagy savakkal kezelt. **b** – A jobb vállról a javítás hiányzik, a javítás körvonalai elmosódottak. **c** – A szemek részletei a szemhéj és írisz nélkül és az erodált orr. A korrózió elektrolízises eltávolítása miatt a felületen nagy lyukak keletkeztek, az arc részletei sérültek. 50-szeres nagyítás. **d** – A sérült száj és áll részletei. A vastagabb zöld lerakódások a szem-gödörben és a szájon az eredeti patina maradványai, a vékonyabb, kupritnyomok nélküli zöld rétegek a nyers fémeken (lásd 6e. ábra) a mesterséges patinázás eredményei. 50-szeres nagyítás. **e** – Dendritok, a hátsó részen végzett elektrolízis nyomai. A kisebb lyukakat a már hiányzó ólomgömbök okozták, a nagyobb mélyedések korróziós lyukak. 50-szeres nagyítás. (Fotók: A. Giunlia-Mair)

The Bacchus bust from the legionary fortress of Brigetio (HNM Inv. no. 3.1944, **Fig. 7a**) highlights a different difficulty that is often encountered when studying or analysing pieces from older collections. Repairs, additions and amendments represent a problem if the reconstructed parts cannot be distinguished from the original alloy, either because they were coated or repatinated with acidic solutions of copper salt solutions, or simply – in the case of ancient repairs – because the surface is covered by a natural patina that disguises the patch. In this case, a raking light had to be employed to evidence on the photos of this Bacchus bust the repair covered by both a natural patina and a layer of conservation resin (**Fig. 7b**). The analysis showed that the composition of the bust and that of the repair are different, with the bust being of copper with 6.7 weight% tin and 18 weight% lead, while the patch only contained 6.2 weight% tin and 7.6 weight% lead. Nevertheless, as no difference in

the patina can be detected, except for a slightly more polished aspect, this repair seems to be ancient. Had only the area on the breast been analysed, it would have given wrong results.

In the case of a Minerva statuette in the Hungarian National Museum (inv.no.105.1895.4, **Fig. 8a**) the situation is again different. The right arm holding the spear is missing and the statuette is rather corroded and covered with an artificial dark patina, i.e. a coating containing iron and nickel, possibly applied twice: the first time as black layer and then a brown layer on top (**Fig. 8b**). The body is leaded bronze with 8.9 weight% Sn and 4.3 weight% Pb, but the disproportionately thin left arm contains high zinc and is definitely a modern reconstruction made of gunmetal. The shield held by the left hand was completely re-done with resin and made of a modern gunmetal or quaternary alloy: copper containing tin, lead and zinc.



Fig. 7.: Bacchus bust (HNM n. 3.1944.) **a** – The alloy is Cu with 6,7 weight% Sn and 18 weight% Pb. The bust still retains most of the natural patina, covered by conservation resin. **b** – The ancient repair (Cu with 6.2 weight% Sn and 7.6 weight% Pb) on the right side of the bust, under the natural patina, was evidenced with raking light for the photo. (Photo A. Giunlia-Mair)

7. ábra: Bacchus büsztje (MNM Ltsz. 3.1944). **a** – A bronzötvözet 6,7 tömeg% ónt és 18 tömeg% ólmot tartalmaz. A patina nagy része természetes, a restaurálás során gyantával borítva. **b** – A büszt jobb oldalán sűrűfényben jól látszik az ókori javítás (réz 6,2 tömeg% ónnal és 7,6 tömeg% ólommal) a természetes patina alatt. (Fotó: A. Giunlia-Mair)



Fig. 8.: Minerva statuette HNM n. 105.1895.4. **a** – Front (right) and back (left). Right arm and spear missing, left arm and shield reconstructed with a quaternary alloy and conservation resins, while only the left hand and perhaps the top of the shield belong to the original casting.

b – Detail of the left hand, which lost part of its patina and coating, showing various layers: red cuprite, green malachite, a layer of black coating and the last brown coating applied on the entire surface of the statuette. X 50 magnification. (Photo A. Giunlia-Mair)

8. ábra: Minerva szobor (MNM Ltsz. 105.1895.4) **a** – Előlnézet (jobbra) és hátulnézet (balra). A jobb kar és a lándzsa hiányzik, a bal kar és a pajzs négykomponensű ötvözetből rekonstruálva, gyantanyomokkal, csak a bal kéz és esetleg a pajzs teteje tartozik az eredeti szoborhoz.

b – A bal kéz részlete. A patina és a bevonat nagy része már eltűnt, különböző rétegek láthatók: vörös kuprit, zöld malachite, a fekete bevonat egy része és a végső barna bevonat, amit a szobor teljes felületén alkalmaztak. (Fotó: A. Giunlia-Mair)

Formation of corrosion compounds from restoration materials

A last point to be touched upon in this paper is that often materials employed in the conservation of artifacts can alter and produce corrosion compounds. This phenomenon has not been observed on the pieces examined for this research, but it has been widely studied and it is important to mention this problem as well. For instance, compounds containing copper acetate have been identified on archaeological copper-based items. The sources of this alteration are not only the ammonium acetate, widely employed for artificial patination on stripped objects, but also acetic acid used for cleaning, cellulose acetate resins used in the past as adhesives or in lacquer, and vinyl acetate and polyvinyl acetate as well. Even Paraloid, commonly used since the 50ies of the last century, can promote corrosion that penetrates deeply into the metal, if it is applied over acidic remains from previous treatments or on small copper chloride formations caused by other factors (Paterakis 1999). Numerous materials used in the past can contribute to the formation of corrosion products and this should also be kept in mind when studying older collections.

Conclusions

This paper addressed only a few of the various problems which analysts face when working on old collections, and not only on statuettes. As discussed above, analysing statuettes coated with 19th century lacquer without recognizing the presence of iron and nickel-based pigments – or (in some other cases) iron-manganese-based pigments – employed for the colouring of the artificial patina would lead to enhanced results of these elements. This, in turn, might create the false impression that the copper employed for these items contains distinct trace elements, possibly suggesting a different provenance for this group of objects.

The electrolytic treatments, extensively employed in the 19th and in some places even into the 1970s, would on their side result in enhanced zinc results on the surface of the treated objects. Similarly, treatments involving strong acids would remove from the surface alloying elements more reactive than copper in the electrochemical series, such as tin and lead, leaving voids, compromising surface integrity and causing too low analytical results for these elements.

Between the 17th and the 19th centuries many more materials were used to cover the surface and imitate a natural patina. In the 20th century, electrolytic treatments used tin and aluminium, not only zinc, also affecting the data, in this case by enhancing the tin results.

It is also important to mention that patina imitations and coatings often consist of several layers of different materials applied at different times. Good examples are famous statues like the Idolino (Iozzo 1999) or the Chimaera from Arezzo (Nicosia & Diana 1992; Iozzo 2009; Siano et al. 2012, 202–204), as well as several the statuettes from Pompeii (Giunlia-Mair 2022a; 2022b). This means that the different coatings applied on the surface might contain a variety of elements that might have a significant impact on surface analyses. Unfortunately, in recent years, the diffusion of portable XRF models, the famigerate “pistols”, used by people with no experience and without any knowledge of ancient metallurgy, produced a plethora of patently wrong data in the archaeological literature.

It is important for both, restorers and analysts, to be aware of the many pitfalls possible with pieces from ancient collections. Understanding the conservation processes applied in the past centuries represents a pivotal point for the studies of ancient metallurgy, but also for evaluation of the preservation conditions of bronze statuettes and copper-based objects in general, and it greatly helps by providing scientific information when deciding the most suitable conservation procedures of collection pieces. Furthermore, it assists archaeologists in understanding the real significance of the analytical data and in the interpretation of the items. Often determining whether an attribute was replaced or repaired in modern times or in antiquity can be quite a challenge.

John Ruskin, the prominent 19th-century English art critic, writer, and thinker profoundly influenced ideas on art, architecture, and preservation and believed that the original material of an artwork, even if decayed, should be respected, because alteration is part of its history. So, in the case of bronze sculptures, patina and corrosion were not blemishes to be “cleaned up” but markers of age and authenticity that should be preserved, not removed. In his influential book *The Seven Lamps of Architecture* he wrote a section titled the “Lamp of Memory,” and argued that signs of time should be retained, and integrity, authenticity, and memory in objects and art should be valued. Living in the Romantic period, Ruskin considered time itself as the artist (Ruskin 1849).

Considering the outcome of some “restorations” of the last few centuries, one feels that Ruskin was indeed right and can only agree with him. In his book he was mainly referring to architecture, but his idea stretched to all historic objects. He stated, “Do not restore. Restore is to destroy. That spirit which should have preserved the work in the first place, should continue to watch over its decay.” and also: “It is impossible, as impossible as to raise the dead, to restore anything that has ever been great or beautiful...” (Ruskin 1880, Chapter IV, 242).

Luckily, over the last half century at least, conservation has increasingly shifted to favouring minimal intervention, and preservation more than removal.

Contribution of authors

Alessandra Giunlia-Mair Investigation, Methodology, Formal analysis, Writing – Original Draft, Review & Editing. **Bartus Dávid** Investigation, Funding acquisition, Project administration, Writing – Original Draft, Review & Editing.

Acknowledgements

This research was supported by National Research Development and Innovation Office, FK131556.

References

- ANTONACCI SANPAOLO, E., BENTINI, J., CORRADIN, E., GUALANDI, G. & ROSATI, R. (1992): La piccola plastica bronzea della collezione Estense di Modena: dati analitici, storico-artistici e la loro elaborazione computerizzata. In: ANTONACCI SANPAOLO, E., ed., *Archeometria, ricerche e prospettive*. GLUEB, Bologna, 653–689.
- ANTONACCI, SANPAOLO, E., FOLLO, L. & GUALANDI, G. (1993): Bronzetti figurati antichi del Museo Provinciale d’Arte di Trento. In: *Archeologia delle Alpi*. Provincia Autonoma di Trento, Soprintendenza per i beni culturali - Ufficio Beni archeologici, Trento, 145–192.
- ASSING, S.P.A. (2020): *Assing Surface Monitor and Surface Monitor 2.0, User’s Manual*. Assing S.P.A. Monterotondo, Roma.
- BAYLEY, J. (1998) The production of Brass in Antiquity with Particular Reference to Roman Britain. In: CRADDOCK, P.T., ed., *2000 Years of Zinc and Brass. British Museum Occasional Paper 50*, London, 7–26.
- BUCHNER, G. (1914): *Die Metallfärbung und deren Ausführung (chemische, elektrochemische und mechanische Metallfärbung)*, M. Krayn Verlag, Berlin, 288 pp.
- CALEY, E.R. (1964) *Oreichalcum and Related Ancient Alloys*, American Numismatic Society, Notes and Monographs **151**, New York, 115 pp.
- CAYLUS, A.C.Ph. (1752–1755): *Recueil d’antiquités égyptiennes, étrusques, grecques, romaines et gauloises, vol. I–VI*. Tillard N.M., Paris, 571 pp.
- CRADDOCK, P.T. (1998): Zinc in Classical Antiquity. In: CRADDOCK, P.T., ed., *2000 Years*

of Zinc and Brass. *British Museum Occasional Paper* 50, British Museum, London, 1–6.

CRADDOCK, P.T. & GIUMLIA-MAIR, A. (1993): Beauty is skin deep: evidence for the original appearance of classical statuary. In: LA NIECE, S. & CRADDOCK, P., eds., *Metal Plating and Patination. Cultural, technical & historical developments*. Butterworth-Heinemann, London, 30–38.

CRADDOCK, P.T. & ECKSTEIN, K. (2003): Production of Brass in Antiquity by Direct Reduction. In: CRADDOCK, P.T. & LANG, J.L., eds., *Mining and Metal Production through the Ages*. British Museum Press, London, 216–230.

DAVIES, O. (1935): *Roman Mines in Europe*. Oxford University Press, Oxford, 291 pp.

GIUMLIA-MAIR, A. (1993): Il caso di Industria, la metallurgia del bronzo e Plinio. *Studi su Industria. Quaderni della Soprintendenza Archeologica del Piemonte* 11 76–97.

GIUMLIA-MAIR, A. (1996): Roman Copper-based Finds from a Slovenian Settlement. *Bulletin of the Metals Museum, Sendai Japan* 25 48–63.

GIUMLIA-MAIR, A. (2002): Analisi. In: *I tesori del mare*. Museo Civico di Storia Naturale, Comune di Trieste, Trieste, 6–9.

GIUMLIA-MAIR, A. (2022a): Glanz der Bronze. Zur Kunst der Metall- und Oberflächen-Bearbeitung. In: BIELFELDT, R., EBER, J., BOSCHE, S., LUTZ, A. & KNAUß, F., eds., *Neues Licht aus Pompeji*, Nünnerich-Asmus Verlag, Oppenheim, 89–101.

GIUMLIA-MAIR, A. (2022b): Ergänzungen, Reproduktionen oder Fälschungen? In: BIELFELDT, R., EBER, J., BOSCHE, S., LUTZ, A. & KNAUß, F., eds., *Neues Licht aus Pompeji*, Nünnerich-Asmus Verlag, Oppenheim, 342–347.

GIUMLIA-MAIR, A. (2025): Metallurgical Innovations at the Time of Julius Caesar and Augustus. In: CIPOLLA, N., LAGATTA, A.F., WEDDLE LIVINGSTON, C., SCHERTZ, P.J.M., SPINELLI, A. & YEOMANS, S.K., eds., *Why Ancient Objects Matter, Greek and Roman Art and Materiality from Antiquity to the Present*. De Gruyter, 359–378.

<https://www.perlego.com/book/4939016/why-ancient-objects-matter-greek-and-roman-art-and-materiality-from-antiquity-to-the-present-pdf>

GIUMLIA-MAIR, A., FERRENCE, S.C. & BETANCOURT P.P. (2015): Metallurgy of the Copper-based Objects from Gournia, East Crete. In: HAUPTMANN, A. & MODARRESSI-TEHRANI,

D., ed., *Archaeometallurgy in Europe III, Proceedings of the 3rd International Conference*. Deutsches Bergbau-Museum Bochum, June 29 – July 1, 2011, Der Anschnitt 26, Bochum, 145–153.

GIUMLIA-MAIR, A., FERRENCE, S.C. & BETANCOURT, P.P. (2023): Data from X-ray Fluorescence Analysis. In: BETANCOURT, P.P. FERRENCE, S.C. & GIUMLIA-MAIR, A., eds., *Metal Objects from Gournia*, INSTAP Academic Press, Philadelphia, 13–20.

HELMIG, D., JACKWERTH, E. & HAUPTMANN, A. (1989): Archaeometallurgical fieldwork and the use of a portable X-ray spectrometer. *Archaeometry* 31(2) 181–191. <https://doi.org/10.1111/j.1475-4754.1989.tb01013.x>

HUGHES, R. & ROWE, M. (2009): *The Colouring, Bronzing and Patination of Metals*. Thames and Hudson, London, 372 pp.

IOZZO, M. (1999): “...qual era tutto rotto”. *L'enigma dell'Idolino di Pesaro Indagini per un restauro*. Nuova Grafica Fiorentina, Firenze, 96 pp.

IOZZO, M. (2009): *La Chimera di Arezzo*. Ministero per i Beni e le Attività Culturali, Soprintendenza per i Beni Archeologici, Edizioni Polistampa, Firenze, 51 pp.

ISTENIČ, J. & ŠMIT, Ž. (2007): The beginning of the use of brass in Europe with particular Reference to the southeastern Alpine region. In: LA NIECE, S., HOOK, D. & CRADDOCK, P.T., eds., *Metals and Mines: Studies in Archaeometallurgy*. London, 140–147.

JANSEN, M., FERRENCE, S.C., GIUMLIA-MAIR, A. & BETANCOURT, P.P. (2023), Data from Investigation of «Zinc-Rich» Copper-Based Artifacts with ESEM-EDS. In: BETANCOURT, P.P., FERRENCE, S.C. & GIUMLIA-MAIR, A., eds., *Metal Objects from Gournia*. INSTAP Press, Philadelphia, 21–23.

LUTZ, J. & PERNICKA, E. (1996): EDXRF analysis of ancient copper alloys. *Archaeometry* 38(2) 313–323. <https://doi.org/10.1111/j.1475-4754.1996.tb00779.x>

MAIER, A. & PELTZ, U. (2013): “ein dauerndes (...) Andenken“ – Axel Kreftings Reduktionsmethode. Anwendungsgeschichte an der Berliner Antikensammlung und ihre analytische und experimentelle Betrachtung. *Archäologie und Restaurierung* 6 19–35.

MENDOZA CUEVAS, A. & PEREZ GRAVIE, H. (2011): Portable energy dispersive X-ray fluorescence and X-ray diffraction and radiography system for archaeometry. *Nuclear Instruments and Methods in Physics Research A* 633 72–78. <https://doi.org/10.1016/j.nima.2010.12.178>

- NICOSIA, F. & DIANA, M. (1992): *La Chimera di Arezzo*. Soprintendenza Archeologica della Toscana, Firenze, 140 pp.
- PATERAKIS, A. (1999): The hidden secrets of copper alloy artefacts in the Athenian Agora. In: GREENE, V. & KAPLAN, E., eds., *Objects Specialty Group postprints*. American Institute for Conservation of Historic and Artistic Works. Objects Specialty Group, Washington DC, 70–76.
- PELTZ, U. (2021): *AES AETERNUM, Die Restaurierungsgeschichte der Bronzen aus Berlins Antikensammlung, I-II*. Verlag des Römisch-Germanischen Zentralmuseums, Mainz, 936 pp. <https://doi.org/10.11588/propylaeum.1182>, <https://doi.org/10.11588/propylaeum.1231>
- PICON M., BOUCHER S. & CONDAMIN J. (1966): Recherches techniques sur des Bronzes de Gaule Romaine, 1. *Gallia* **34** 189–214.
- PICON M., BOUCHER S. & CONDAMIN J. (1967): Recherches techniques sur des Bronzes de Gaule Romaine, 2. *Gallia* **35** 153–168.
- PICON M., BOUCHER S. & CONDAMIN J. (1968): Recherches techniques sur des Bronzes de Gaule Romaine, 3. *Gallia* **36** 245–278.
- PFISTERER-HAAS, S. (2022): Phallos, Feuer, Klang. Tinnabula aus Pompeji. In: BIELFELDT, R., EBER, J., BOSCHE, S., LUTZ, A. & KNAUB, F., eds., *Neues Licht aus Pompeji*. Nünnerich-Asmus Verlag, Oppenheim, 318–320.
- POPOV, K.I., KEČA, D.N. & ANDJELIĆ, M.D. (1978): Electrodeposition of Zinc on Copper from Alkaline Zincate Solutions. *Journal of Applied Chemistry* **8** 19–23. <https://doi.org/10.1007/BF00615389>
- RATHGEN, F. (1898): *Die Konservierung von Alterthumsfunden*. Handbücher der königlichen Museen zu Berlin 7, Berlin, 147 pp.
- RATHGEN, F. (1905): *The preservation of Antiquities. A Handbook for Curators*. University Press, Cambridge, 176 pp.
- RIEDERER, J. (2002a): The use of standardized copper alloys in Roman metal technology. In: GIUMLIA-MAIR, A. ed., *I Bronzi Antichi: Produzione e tecnologia*. Atti del XV Congresso Internazionale sui Bronzi Antichi, Grado-Aquileia, Edizioni M. Mergoïl, Montagnac, 284–291.
- RIEDERER, J. (2002b): Die Metallanalyse der römischen Statuetten des Römisch-Germanischen Museums in Köln. In: GIUMLIA-MAIR, A. ed., *I Bronzi Antichi: Produzione e tecnologia*. Atti del XV Congresso Internazionale sui Bronzi Antichi, Grado-Aquileia, Edizioni M. Mergoïl, Montagnac, 292–300.
- ROBOTTI, S., RIZZI, P., SOFFRITTI, C., GARAGNANI, G.L., GRECO, CH., FACCHETTI, F., BORLA, M., OPERTI, L. & AGOSTINO, A. (2018): Reliability of portable X-ray Fluorescence for the chemical characterisation of ancient corroded copper tin alloys. *Spectrochimica Acta, Part B: Atomic Spectroscopy* **146** 41–49. <https://dx.doi.org/10.1016/j.sab.2018.04.017>
- RUSKIN, J. (reprint 1880) *The Seven Lamps of Architecture*. G. Allen ed., London, 288 pp.
- SIANO, S., MICCIO, M., GIAMELLO, M., MUGNAINI, S. & AGRESTI, J. (2012): Journey through the material layers of the Chimaera from Arezzo. In: CIANFERONI, G.C., IOZZO, M. & SETARI, E., eds., *Myth, Allegory, Emblem. The many lives of the Chimaera of Arezzo*. Aracne, Roma, 185–222.
- SOLES, J. & GIUMLIA-MAIR, A. (2018): Metallurgical Habits and Workshop Remains in LMIB Mochlos, East Crete. In: GIUMLIA-MAIR, A. & LO SCHIAVO, F., eds., *Bronze Age Metallurgy on Mediterranean Islands. In honor of Robert Maddin and Vassos Karagheorgis*. Monographies Instrumentum **56**, Edizioni Mergoïl, Drémil-Lafage, 498–519.
- THOMAS, R. (2002): Welche Aussagen erlauben die Materialanalysen der in Köln gefundenen Bronzestatuetten? In: GIUMLIA-MAIR, A. ed., *I Bronzi Antichi: Produzione e tecnologia*, Atti del XV Congresso Internazionale sui Bronzi Antichi, Grado-Aquileia, Edizioni M. Mergoïl, Montagnac, 301–315.
- VIJARATNAM, V., NATTER, H., GRANDTHYLL, S., NEUROHR, J.U., JAKOBS, K., MÜLLER, F. & HEMPELMANN, R. (2017): Unwanted electroless zinc plating on current collectors in zinc air batteries. *ArXiv* ArXiv:1706.05929. <https://doi.org/10.48550/arXiv.1706.05929>
- XU, S., ZHU, Y., XIONG, D., WANG, L., YANG, P. & CHU, P.K. (2017): Zinc Electrodeposition on Polycrystalline Copper: Electrochemical Study of Early-Stage Growth mechanism. *The Journal of Physical Chemistry C* **121/7** 3938–3946. <https://doi.org/10.1021/acs.jpcc.6b12036>

