

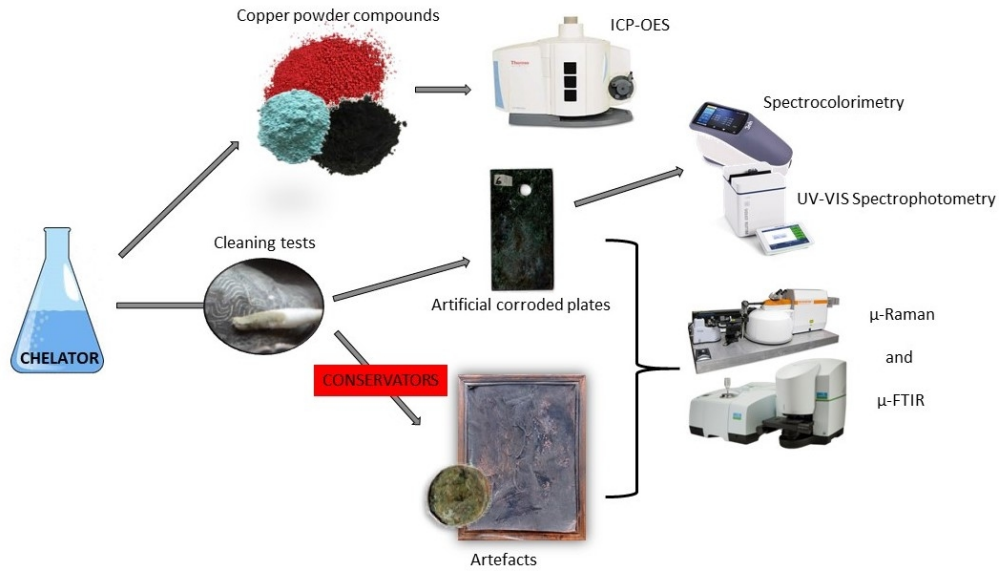


Natural based products for cleaning copper and copper alloys artifacts

Journal:	<i>Natural Product Research</i>
Manuscript ID	GNPL-2021-1243.R3
Manuscript Type:	Research Article
Date Submitted by the Author:	11-Oct-2021
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Keywords:	cleaning, copper, bronze, amino acid, chelator, cultural heritage

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Natural based products for cleaning copper and copper alloys artefacts

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Abstract

Copper alloys objects can deteriorate their conservation state through irreversible corrosion.

Since in the cultural heritage field every artefact is unique and any loss irreplaceable, solutions for conservation are needed.

Hence, there is the necessity to stop the corrosion process with a suitable cleaning and conservation process to avoid further degradation processes without changing its morphological aspect.

Chelating solutions are commonly used in chemical cleaning, mainly sodium salts of ethylenediaminetetraacetic acid (EDTA). However, it is resistant to water purification procedures and is not biodegradable.

The goal of this study was to see if applying an ecologically friendly chelating agent as an alternative to EDTA cleaning procedures for cultural heritage was suitable.

In this study were chosen six natural-based chelators that could be a new green non-toxic alternative to EDTA in corrosion-inhibiting properties.

They were tested for cleaning copper artefacts exposed to atmospheric environment in polluted areas. The study considered four amino acids, a glucoheptonate (CSA) and an industrial green chelator (GLDA). The effectiveness was tested on corrosion copper compounds and on laboratory corroded copper sheets. Finally, the cleaning efficacy was tested on four Roman coins and a modern copper painting. To define the cleaning efficacy, surface analytical investigations have been carried out by means ICP-OES, UV-VIS, μ -Raman, spectrophotometry, XRD and FTIR. Among the amino acids, alanine was the most effective, showing an unaltered noble patina and a good effective copper recovery from corrosion patinas.

Keywords: amino acid; bronze; chelator; cleaning copper; cultural heritage.

1. Introduction

Archaeological artefacts bear witness of human art and creativity used both to produce copper artefacts for daily use and invaluable artworks. Furthermore, they reveal the level of technological expertise and the sophisticated feeling for shape and chromatic effect. A large component of this cultural heritage consists of material cultural assets that are often exposed to harmful long-term effects of environmental pollution, inappropriate handling, and intrinsic chemical–physical instability.

In Cu based alloys the degradation is essentially because of a redox electrochemical reaction that takes place as a consequence of the interaction between the material and the environment. This causes alterations of the chemical–physical properties of the material itself in different ways as a function of the nobility of the metal or of the metallic alloy. The corrosion phenomena may be divided into dry corrosion and wet corrosion with dependence on the environmental conditions. Different forms of attack may affect the metallic artefacts and may be distinguished in two categories: uniform corrosion that proceeds on the overall surface and the more dangerous localised corrosion. Atmospheric corrosion shows generally a uniform character; it occurs when a layer of electrolyte is present on a structure (rain, humidity, etc.). The aggressiveness of the atmosphere is increased by the presence of pollutants such as sulphur dioxides, powder particles, and hygroscopic salts. Then the corrosion of a metallic artefact depends on temperature, pH, oxygen content, amount of salt, etc.

As a result, the alteration products of copper alloys are different in composition and structure and include various species: oxides as cuprite (Cu_2O) and tenorite (CuO); sulphides as chalcocite (Cu_2S) and covellite (CuS) and basic sulphates as brochantite ($\text{Cu}_4(\text{SO}_4)(\text{OH})_6$) and antlerite ($\text{Cu}_3(\text{SO}_4)(\text{OH})_4$) in urban atmosphere; chlorides and hydroxychlorides as atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$); basic green carbonates as malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$) and azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) and oxalates as $\text{Cu}(\text{COO})_2 \cdot n\text{H}_2\text{O}$.

The copper-based artefacts, such as bronzes, sometimes can show resistance to degradation because they are able to develop a layer of chemical compounds called patina that has a barrier action against further degradation. When patina is stable it does not change the appearance of the artefact, on the contrary it makes it unique and unrepeatably. In these cases, patinas are called “noble patinas”, because they give an additional aesthetic value as a symbol of the passage of time. Furthermore, some of

noble patinas can be passivating layers, protecting the artwork from further corrosion (Gettens 1970).

Copper and high-Cu alloys are sensitive to exposure to atmospheric agents: the presence in the environment of aggressive agents, such as hydrogen sulphide (H₂S), carbonyl sulphide (COS) and sulphur dioxide (SO₂), even in small quantities, combined with the presence of high relative humidity (RH), can quickly cause an alteration of the surface. The interaction with polluted atmosphere can generate, with time, strong corrosion phenomena which, if not stopped, can lead to the destruction of the whole artefact.

The most common copper compounds in outdoors bronzes are oxides, including cuprite (Cu₂O) and tenorite (CuO), and sulphates, especially brochantite (Cu₄SO₄(OH)₆). Tenorite and cuprite are the first products to form. Copper salts, usually observed on copper artworks, are formed from the interaction of Cu-oxides and environmental pollutants (Brambilla 2011). Brochantite and other sulphates darken over time, weighing on the aesthetic aspect of the artwork and are generally considered non-noble patinas and they should be removed (Bassini 2012; Brambilla 2011; Rahmouni et al. 2004; Walker 1980).

To preserve an artefact and pass it on to future generations, a cleaning intervention is then required in order to remove the dangerous products and save the artefact (Petiti et al., 2020). The aim of cleaning an artefact is to preserve the noble patinas and to remove non-noble ones. It is therefore necessary to use methods that allow a continuous control and gradualness of the cleaning intervention, to act only on the layers that must be removed (Parisi et al., 2017). Usually, the cleaning is performed mainly through mechanical and chemical methods, and it is precisely on the latter that this work focuses.

Chemical cleaning mainly involves the use of chelating solutions. Among these, sodium salts of ethylenediaminetetraacetic acid (EDTA-Na₂ and EDTA-Na₄) are the most used to remove copper and bronze corrosion patinas (-Xu 2007). Although it is not harmful to people, in recent decades several studies have pointed out that EDTA is not very biodegradable and is resistant to water purification treatments (Masoudi et al., 2020). This is because, EDTA can be involved in the mobility of heavy and radioactive ions and contribute to eutrophication of water. Amino acids have recently been introduced as natural and environmentally friendly chelating agents in a variety of applications for their selective and reversible metal chelating/coordination properties

(Dolev et al., 2020) and their use in cultural heritage conservation for cleaning treatments has been investigated applied to the stone materials (Macchia et al. 2011). Moreover, a biodegradable chelating and cost-effective agent, Dissolvine GL, has been commercialised as a green alternative to EDTA. The product contains L-glutamic acid (from sugar, molasses, corn or rice), which is produced biochemically to yield the pure L isomer. The amino acid is then modified using a proprietary process to produce GLDA (glucamic acid diacetic acid).

The main purpose of the study is introduced an effective and natural cleaning agent for removing copper corrosion patinas. The concept of green was born in recent decades and is based on the research and use of materials and methods that are more respectful to the environment and, at the same time, not harmful to the operators (Koodynska 2011). In the field of cultural heritage conservation, in addition to these two key factors, it is necessary that green products also respect the artworks and its integrity (Dermaj et al. 2015; Faraldi et al. 2017; Faraldi et al. 2014; Macchia et al. 2011; Mezzi et al. 2012). Chemical compounds were then selected based on the following parameters: the complexation capacity on copper ions, optimal pH for complexation and previous test in the conservation of cultural heritage field (Macchia et al. 2011; Miličević & Raos 2006; Varvara et al. 2011; Varvara et al. 2009; Varvara et al. 2009).

In light of the above considerations, this work is aimed to employ natural based chelators for cleaning copper and bronze artefacts. Different chemical compounds, such as amino acids, were tested in laboratory on artificially corroded metal and on original artefacts. The innovative aim of the study is the application of amino acids for the cleaning of bronze artifacts respect to the current systems, The choice to use amino acids and no protein–metal interactions was to have the maximum solubility of the chelate and to control the zwitteronic form with pH, and, at the same time, obtain the maximum chelating power.

2. Results and discussion

2.1. Laboratory Tests

Results of ICP/OES analysis, concerning tests on powdered copper compounds, are reported in percentage of copper recovered from each chelator and for each extraction

times (Figure ~~1~~S4). The concentrations obtained by instrumental measurements have been normalised, taking into consideration the maximum concentration of copper present in each test tube (1000 ppb), corresponding to 100% of extracted copper.

In the case of cuprite (Figure ~~S4~~a), EDTA- $\text{Na}_{2/4}$ is the chelator that showed the highest capacity of copper removal in the long term. Alanine, on the other hand, is the chelator that shows greater difficulty in chelation. Methionine and cysteine show an extraction capacity which decreases over time, due to the formation of a precipitate, blue and yellow respectively.

A greater extraction difficulty by chelators is observed with tenorite (Figure ~~S4~~b). Methionine, cysteine, and CSA extract the most copper from this compound. As in the previous case, the two amino acids mentioned above have an extraction capacity that decreases over time due to the formation of a precipitate blue for methionine and blue/grey for cysteine.

Finally, copper extraction from brochantite seems to be favoured for all chelators (Figure ~~1e~~S4c). Despite this, methionine and cysteine form a precipitate, blue and yellow respectively, which does not allow to reach 100% of the extracting capacity. Furthermore, CSA, compared to the others, has a slower action, reaching extraction of the whole copper after 24 hours.

Two natural based chelators were chosen for the next step according to:

- the effectiveness in the removal of non-noble *patinas* preferring chelators with greater effectiveness in the complexation of copper from brochantite;
- the lowest efficacy in removing noble *patinas* choosing chelating agents with less extraction capacity with cuprite and tenorite;
- the effectiveness especially in the first 30 min (in a conservation process a solution is never kept in contact with the metal surface for long times);
- the absence of secondary chemistry (the chelator is not suitable for conservation purposes).

Based on these considerations, GLDA and alanine were chosen as natural based chelating agents for subsequent tests, together with EDTA- $\text{NA}_{2/4}$ always taken as reference.

2.2 Tests on artificial corroded plates

Once cleaning test were carried out, the concentration of copper collected from the cellulose poultices allowed us to evaluate the effectiveness of each chelator in

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3 cleaning the plates. In the cleaning of LI plates with a Cu oxide *patina* (tenorite) all the
4 chelators showed difficulty in extraction. We note that, in the short term, alanine
5 extracts less copper oxide, although with increasing time it achieves results like those of
6 EDTA- $\text{Na}_{2/4}$. GLDA, on the other hand, is the most effective of all in the removal of
7 tenorite. In the cleaning of plates LII and LIII, made up of non-noble *patinas* of
8 sulphates, all the chelating agents showed a good extraction capacity. Alanine seems to
9 be the one which best extracts sulphates, especially in the short term, but in the long
10 term there are few differences between the three chelators (Figure [S52](#)).

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17 Cleaning tests have been also evaluated through spectro-colorimetric analysis
18 and the results made it possible to underline how all chelators allow the patina removal
19 without restoring the surface to its original appearance. In the case of LI plates, we note
20 that no chelators led to a noticeable variation in the spectra (Figure [S65a](#)). This is linked
21 to the fact that the three chelators, as also highlighted from the previous data, show a
22 difficulty in extracting tenorite. Despite this, it seems that EDTA and especially GLDA
23 have produced a greater variation of spectra, probably since they extract copper from
24 tenorite better than alanine. In the case of LII (Figure [S5bS6b](#)) and LIII (Figure [S5eS6c](#))
25 plates it is noted that EDTA and GLDA involve a variation in the spectral range 600-
26 700 nm region that characterizes the original copper surface. In fact, EDTA and
27 especially GLDA do not act uniformly thereby creating areas in which there is a greater
28 interaction with the original surface. Cleaning with alanine, instead, led to an increase in
29 reflectance for all wavelengths, without however altering the spectrum curve. This
30 means that alanine acted homogeneously over the entire surface of the plate, without
31 approaching the original copper.
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44 **2.3 Test on artefacts**

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47 The μ -Raman spectra allowed the mineralogical characterization of the patinas for both
48 coins (Table S2) and painting (Table S3).

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51 Cleaning of M1 coin was performed with all three chelators (Figure [S4bS7b](#)).
52 However, GLDA and EDTA removed part of the passivating noble *patina* of the
53 artefacts. This result is due both for the high ability of the two chelators to extract
54 copper and because of the patinas were quite thin. The low thickness is probably due to
55 the artificial treatment previously hypothesised. Based on the results obtained, M1, M2
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and M3 have been cleaned only with alanine, which has shown greater inalterability of noble *patinas* (Figure S4bS7b).

Cleaning of the Cu-painting has been carried out not only with the three chelators (alanine, EDTA and GLDA) but also with deionised water, as the *patina* was not very coherent in some areas (Figure S83a). However, good results have not been obtained with water, except with the addition of a surfactant, as the *patina* is formed by insoluble compounds. For this reason, a further test has been carried out after washing the entire work with deionised water. GLDA in the first cleaning test produced a shiny and metallic surface. This means that GLDA reach the original surface of artefacts. Consequently, only the tests with alanine and EDTA were repeated after washing with deionised water (Figure S83b). In both cases, we can notice that chelators effectively remove the *patina*, but in an inhomogeneous way. Despite this, alanine allows for a less glossy surface, due to the greater inalterability of the *patina*.

3. Experimental

~~Chemical compounds were selected based on the following parameters: the complexation capacity on copper ions, optimal pH for complexation and previous test in the conservation of cultural heritage field (Macchia et al. 2011; Miličević & Raos 2006; Varvara et al. 2011; Varvara et al. 2009; Varvara et al. 2009). Chelating agents with an ideal pH lower than 5 and higher than 9 have been discarded since this pH could damage copper and copper alloys. Four amino acids consisting of different functional groups have been chosen: alanine (ALA), cysteine (CYS), methionine (MET), and lysine (LYS). Moreover, two new natural based chelators were also tested: GLDA and CSA (sodium glucoheptonate) (Koodynska 2011; Mehlretter et al. 1953). These compounds were compared with a disodium and tetrasodium EDTA solution, commonly used in the conservation and, for this, taken as reference. Every chelating agent was tested to a concentration of 0.13M (Macchia et al. 2011). Solutions were used at a spontaneous pH, except for GLDA, brought to pH 9 with acetic acid. In fact, considering the stability curve of GLDA complexes, the chelator has an excellent copper complexation just to pH 9 (Begum et al. 2012).~~

~~The study focused on the most common corrosion products in polluted environment: cuprite, tenorite and brochantite minerals (Bassini 2012; Brambilla 2011; Rahmouni et al. 2004; Walker 1980).~~

The best natural based solution (the lowest and the highest efficiencies in the extraction of copper from noble patinas and non-noble ones respectively) was identified through three consecutive steps.

More information about experimental section is found in supplementary materials.

4. Conclusions

The results achieved have provided important information on the complexing capacity of some natural based products against copper and copper alloys corrosion.

Alanine has shown excellent effectiveness against non-noble *patinas*, while preserving the noble ones. Thus, the use of Alanine as a green chelant in conservation applications looks to be a promising green alternative.

As Alanine has been shown to be easily degradable, it is suggested that it be considered as an alternative chelating agent for stabilizing copper corrosion products in the cultural heritage preservation. Furthermore, our findings demonstrate that in the presence of various cupriferous materials Alanine is equivalent to EDTA in terms of chelating effectiveness.

The present study is therefore a first step to begin further studies to increase its use for the archaeological artefacts conservation.

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4 SUPPLEMENTARY MATERIALS5
6 **Natural based products for cleaning copper and copper alloys artifacts**
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Natural based products for cleaning copper and copper alloys artifacts

Copper alloys objects can deteriorate their conservation state through irreversible corrosion. Hence, there is need to block the corrosion action with a suitable cleaning and conservation process to avoid further degradation processes without changing its morphological aspect. In this study, six natural based chelators were tested for cleaning copper artefacts exposed to atmospheric environment in polluted areas. The study considered four amino acids, a glucoheptonate (CSA) and an industrial green chelator (GLDA). The effectiveness was tested on corrosion copper compounds and on laboratory corroded copper sheets. Finally, the cleaning efficacy was tested on four Roman coins and a modern copper painting. To define the cleaning efficacy, surface analytical investigations have been carried out by means ICP-OES, UV-VIS, μ -Raman, spectro-colorimetry, XRD and FTIR. Among the amino acids, alanine was the most effective, showing unalteration of the noble patina and a good effective copper recovery from corrosion patinas.

Keywords: amino acid; bronze; chelator; cleaning copper; cultural heritage.

Materials and Methods **Experimental**

Chelating agents with an ideal pH lower than 5 and higher than 9 have been discarded since this pH could damage copper and copper alloys. Four amino acids consisting of different functional groups have been chosen: alanine (ALA), cysteine (CYS), methionine (MET), and lysine (LYS). Moreover, two new natural based chelators were also tested: GLDA and CSA (sodium glucoheptonate) (Koodynska 2011; Mehlretter et al. 1953). These compounds were compared with a disodium and tetrasodium EDTA solution, commonly used in the conservation and, for this, taken as reference. Every chelating agent was tested to a concentration of 0.13M (Macchia et al. 2011). Solutions were used at a spontaneous pH, except for GLDA, brought to pH 9 with acetic acid. In fact, considering the stability curve of GLDA complexes, the chelator has an excellent copper complexation just to pH 9 (Begum et al. 2012).

The study focused on the most common corrosion products in polluted environment: cuprite, tenorite and brochantite minerals (Bassini 2012; Brambilla 2011; Rahmouni et al. 2004; Walker 1980).

The best natural based solution (the lowest and the highest efficiencies in the extraction of copper from noble patinas and non-noble ones respectively) was identified through three consecutive steps.

Reagents and equipments

The following chemicals were used in this work: EDTA-Na₂ (Sigma-Aldrich); EDTA-Na₄ (Sigma-Aldrich); alanine (Alfa Aesar); cysteine (Alfa Aesar); methionine (Alfa Aesar); lysine (Carlo Erba); Dissolvine GLPDS (Eigenmann & Veronelli); Dissolvine CSA (Specialities); copper (I) oxide (Carlo Erba); copper (II) oxide (Carlo Erba);

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3 copper (II) sulfate (Carlo Erba); copper (II) sulfate pentahydrate (Sigma-Aldrich);
4 sodium hydroxide (Alfa Aesar); ammonium sulfate (Alfa Aesar); ammonium chloride
5 (Alfa Aesar); sodium nitrate (Alfa Aesar); hydrogen nitrate (Sigma-Aldrich); sodium
6 acetate (Alfa Aesar); sodium formate (Alfa Aesar).
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11
12 The following equipments were used for the analysis: diffractometer Siemen
13 5000 model, with Cu K α radiation filtered with Ni ($\lambda = 0.154056$); thermostatic bath
14 Dubnoff M428-BD; ICP/OES spectrometer Icap 6300 Duo spectrum; micro-Raman
15 spectrometer Renishaw 2000 equipped with a 785 laser; FTIR spectrometer Perkin
16 Elmen Spotlight Spectrum 400 FT-IR-NIR microscope; UV-VIS spectrophotometer
17 Mattler toledo UV5Bio; spectro colorimeter 3nh Y3060.
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26 In this study were used also: cellulose acetate filter (Minisart); powdered
27 Cellulose (Arbocel BC1000).
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32 **Laboratory Tests**

33
34 In laboratory, extraction effectiveness of different chelators with the three powdered
35 copper compounds (cuprite, tenorite and brochantite) was defined. To obtain powdered
36 brochantite it has been necessary to synthesize it, according to the synthesis proposed
37 by Vilminot et al. (2005). A powder sample has been analysed by XRD, which certified
38 the actual synthesis of brochantite.
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46 The procedures carried out for the extractive tests can be summarised as follows:
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48 each copper compound has been weighed and putted in a glass flask; equal volumes of
49 extracting solutions have been added ($C_{Cu}=100$ ppm for every test). The extraction tests
50 have been performed in a thermostatic bath with continuous stirring 25°C and 200
51 strokes. An aliquot of 0.1 ml has been extracted from each flask at different times (30,
52 120, 300, 1440 min), introduced in a test tube after filtration trough 0.2 μ m cellulose
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3 acetate filter, and diluted 1/10 with deionised water. The resulting solutions have been
4
5 analysed by ICP / OES.
6
7

8 9 ***Tests on laboratory corroded plates***

10
11 To simulate a degraded bronze object, three types of patinas have been reproduced on
12
13 copper plates, previously polished, whose dimensions are 2.5x5x0.05 cm (Chiavari et
14
15 al. 2009). As well as the procedure performed by Brambilla L., 2011 e Chiavari C. et
16
17 al., 2009, the plates were not treated in any other way before being subjected to
18
19 chemical patination (Brambilla 2011; Chiavari et al. 2009; Vilminot et al. 2005). Plates
20
21 have been divided into three groups (LI, LII, LIII), depending on the simulated patina.
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23
24

- 25
26
27 • In LI plates, tenorite patina has been reproduced with the method proposed by
28
29 Zheng et al. (2014). Plates have been immersed in 4 M NaOH aqueous solution
30
31 for two days, in atmospheric environment. The same procedure has been applied
32
33 twice, renewing the alkaline solution.
34
35
- 36
37 • In LII plates, corrosion of atmospheric environment has been simulated with the
38
39 method proposed by Marušić et al. (2011). Plates have been immersed in 15 mM
40
41 of CuSO₄ aqueous solution for 2 weeks at room temperature.
42
- 43
44 • In LIII plates, burial environment corrosion has been simulated with the method
45
46 proposed by Angelini et al. (2007). Plates have been buried in 60g of ground
47
48 (30g above and 30g below) for 1 months. The soil has been subjected to
49
50 hydration with the solution proposed by Brambilla (2011), by simulating the
51
52 acid rain.
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56 Obtained patinas have been characterised through micro-Raman and micro-
57
58 FTIR spectroscopy.
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3 All the treated plates have been subsequently subjected to cleaning tests by
4 using the two best natural based chelators of laboratory tests and EDTA- $\text{Na}_{2/4}$ (as the
5 reference). The cleaning has been carried out putting in contact plates with 5 g of
6 cellulose pulp, wet with 25 ml of extracting solution. Each cellulose poultice has been
7 in contact with the surface for different extraction times: 10, 20, 60, 120 min. After the
8 removing, every poultice has been introduced in test tube containing 10 ml of deionised
9 water. The resulting solutions have been analysed by UV-VIS spectrophotometry, to
10 know the concentration of copper extracted during cleaning tests. After each cleaning
11 test, artificial corroded plates have been washed with deionised water. To identify the
12 concentration of extracted copper during cleaning test has been necessary to obtain
13 calibration curves for each chelator. For this, four standards (50, 100, 150, 200 ppm)
14 have been performed from a solution of 1000 ppm of Cu. To evaluate the cleaning
15 effect, colorimetric measurements have been also performed, before and after the
16 treatment, on 10 different areas of the plates and data have been averaged.

36 ***Tests on artworks***

37
38 For cleaning tests, bronze Roman coins of different types belonging to a private
39 collection (Figure S1a) and a copper painting (Figure S2) have been selected. The
40 copper artefact, belonging to the private collection of the YOCOCU Organization and
41 entitled "Tramonto estivo" is attributable to the second half of the 20th century. The
42 author is unknown (illegible signature). The presence of non-corroded areas made it
43 possible to hypothesize that the artwork had a copper-like appearance. Patinas of both
44 have been characterised by μ -Raman spectroscopy.

45
46 Cleaning tests on the artefacts have been carried out by means of cellulose pulp
47 wet with extracting solution and with the help of tampons, combining chemical and
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3 mechanical methods. After each cleaning test, the surface has been washed with
4
5 deionised water. The effectiveness of the cleaning has been evaluated according with
6
7 the conservators consideration.
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10 11 **Raman characterisation**

12 13 14 *Tests on artificial corroded plates*

15
16
17 Artificial corrosion led to the formation of insoluble corrosion patinas, extending over
18
19 the entire surface of plates (Figure S3). μ -Raman spectroscopy has allowed to
20
21 characterise the patinas of LI and LII plates (Table S1). In LI plate, tenorite was found,
22
23 in LII plate chalcantite and chalcocyanite, μ -FTIR spectroscopy highlighted the
24
25 presence of brochantite on LIII patina (Figure S4). The compounds found in every type
26
27 of artificial corroded plate reflect the anions and cations present in the solutions used to
28
29 induce artificial corrosion.
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32
33

34 35 *Test on artifacts*

36
37 In the M1 coin a red cuprite patina and a green one of malachite and copper
38
39 acetate were found. In the M2 coin and in the M3 coin a blue-green patina consisting of
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41 atacamite, tenorite and copper acetate (Table S2). The presence of copper acetate has
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43 allowed us to hypothesize that coins were artificially treated, as this corrosion product
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45 does not form in natural environments.
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49 The characterisation of the painting made it possible to discover that it had a
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51 patina of tenorite, calcite, pyrite, and carbonaceous particulate (Table S3).
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Tables

Table S1. Results of micro-Raman spectroscopy. Summary of the bands collected, of the compounds found and of the references (literature and RUFF databases) used for identification.

Plate	Raman bands (cm ⁻¹)	Compound	Reference
LI	131.4, 149.2, 298.5, 518.6	Tenorite	R050098
LII	129, 210.9, 453.7, 606.1, 982.2, 1013.6, 1045.3, 1205.3	Chalcanthite, Chalcocyanite	R050354, Buzgar et al. (2009) (chalco-cyanite)

Table S2. Results of micro-Raman spectroscopy on coins. Summary of the bands collected, of the compounds found and of the references (literature and RUFF databases) used for identification.

Coin	Raman bands (cm ⁻¹)	Compound	Reference
M1A	112.8, 149.6, 300.3, 520.6, 622	Cuprite	R050384
M1B	151.2, 169.8, 177.7, 215.5, 268, 354.2, 431.7, 534 1051.8, 1084.4, 1488.8, 1576.6	Malachite, Copper (II) acetate	R050531; Quiles F. et al. (1998) (acetate)
M2A	110.5, 154.6, 181.9, 211.3, 373, 517.9, 625.8, 830.8, 923.2, 973.6, 1206.7, 1416, 1532, 1633	Atacamite, Tenorite, Copper (II) acetate	R050098, R060071; Marucci G. <i>et al.</i> (2018) e Quiles F. et al. (1998) (acetate)
M2B	114.7, 156.7, 175.6, 215.5, 358.3, 524.2 828.7, 921, 969.5, 1200.4, 1427, 1628	Atacamite, Tenorite, Copper (II) acetate	R050098, R060071; Marucci G. <i>et al.</i> (2018) e Quiles F. et al. (1998) (acetate)
M3	110.5, 156.7, 177.7, 215.5, 385.6, 522.1, 923.2, 975.7, 990.4, 1206.7, 1418, 1532.2, 1633	Atacamite, Tenorite, Copper (II) acetate	R050098, R060071; Marucci G. et al. (2018) e Quiles F. et al. (1998) (acetate)

Table S3. Results of micro-Raman spectroscopy on coins. Summary of the bands collected, of the compounds found and of the references (literature and RUFF databases) used for identification.

Painting area	Raman bands (cm ⁻¹)	Compound	Reference
Q1	146.6, 172.9, 195.3, 284.0, 333.6, 520.6, 627.1, 844.7	Tenorite, Chalcocite	R060071; R120090
Q2	144.3, 163.5, 185.4, 515.7, 630.2, 332.9, 331.1, 358.7, 534.6, 801.8, 860.4, 1310.8, 1566.2	Tenorite, Pyrite, Carbon particle	R060071; R050190; Stitch S. et al. (1998) (particle)
Q3	281.9, 318.7, 335.2, 342.5, 366.2, 531.1, 752.6, 839.3, 854.4, 1347.9, 1606.5	Pyrite, Chalcocite, Carbon particle	R050190; R120090; Stitch S. et al. (1998) (particle)

Figures



Figure S1. “Tramonto estivo”, belonging to the private collection of the YOCOCU organization. The painting represents a kneeling woman in high relief.

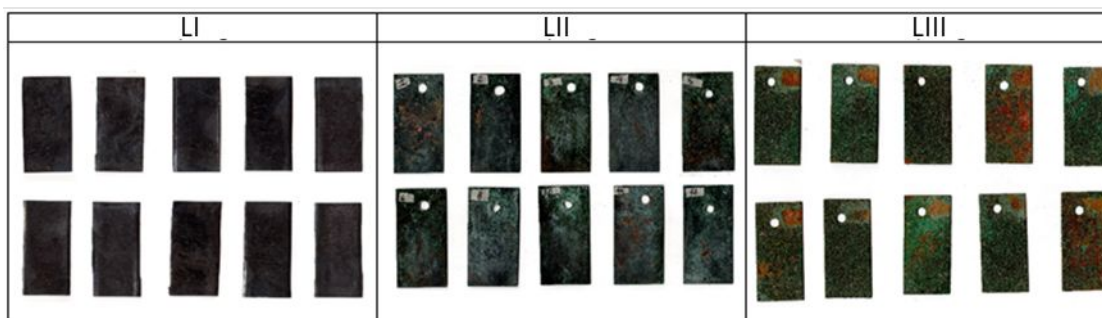


Figure S2. Results of the artificial corrosion of copper plates. Tenorite patina, atmospheric environment corrosion and burial degradation have been simulated respectively on LI, LII and LIII plates.

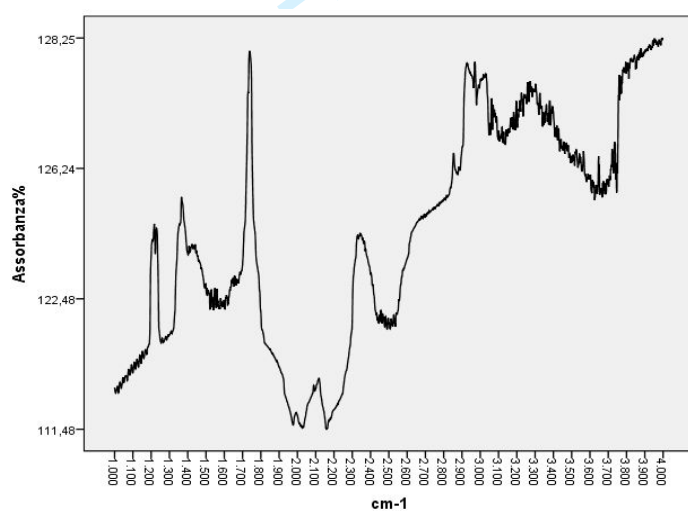


Figure S3. Spectrum collected through micro-FTIR spectroscopy on LIII plates. Brochantite has been identified.

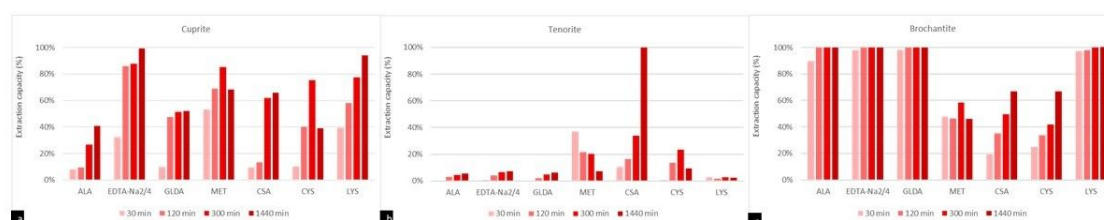


Figure S4. The histograms represent the percentages of copper extracted from cuprite (a), tenorite (b), and brochantite (c) by chelators in the different extraction times ($2.5 < SD < 10$).

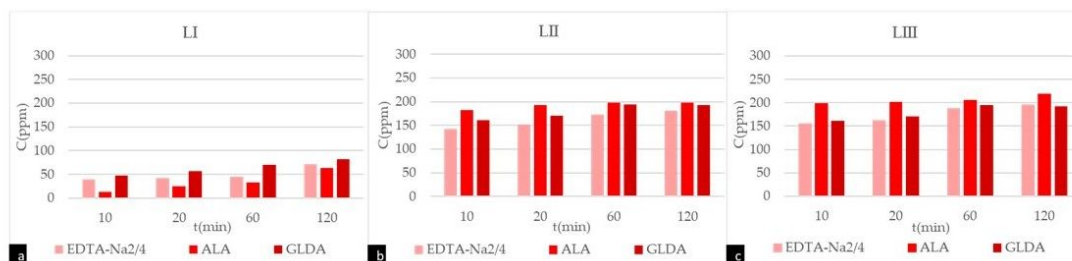


Figure S5. Concentration of copper extracted, through cellulose pulp wet with different chelators, during cleaning test of LI (a), LII (b) and LIII (c). Every test has been performed in different times ($1.5 < SD < 5$).

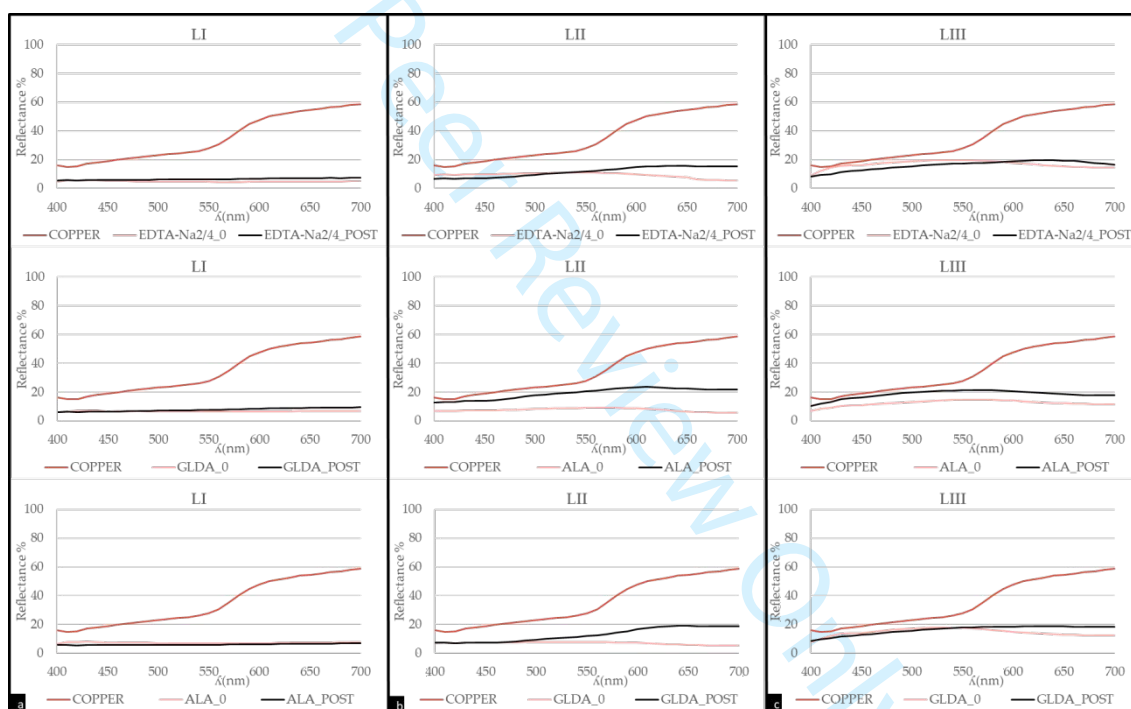


Figure S64. Spectra collected with spectro-colorimeter on LI (a), LII (b) and LIII (c) plates. Graphs show variations in surfaces reflectance before degradation (COPPER), after degradation (CHELATOR_0) and after cleaning tests (CHELATOR_POST). Alanine, EDTA-Na₂/4 and GLDA are the chelators used.

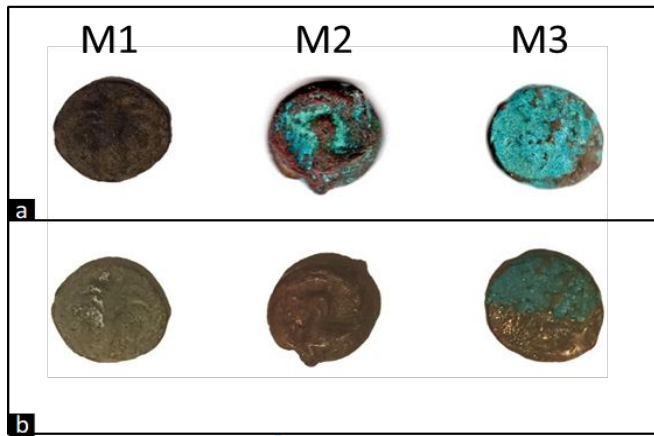


Figure S75. Coins before (a) and after (b) cleaning treatment.

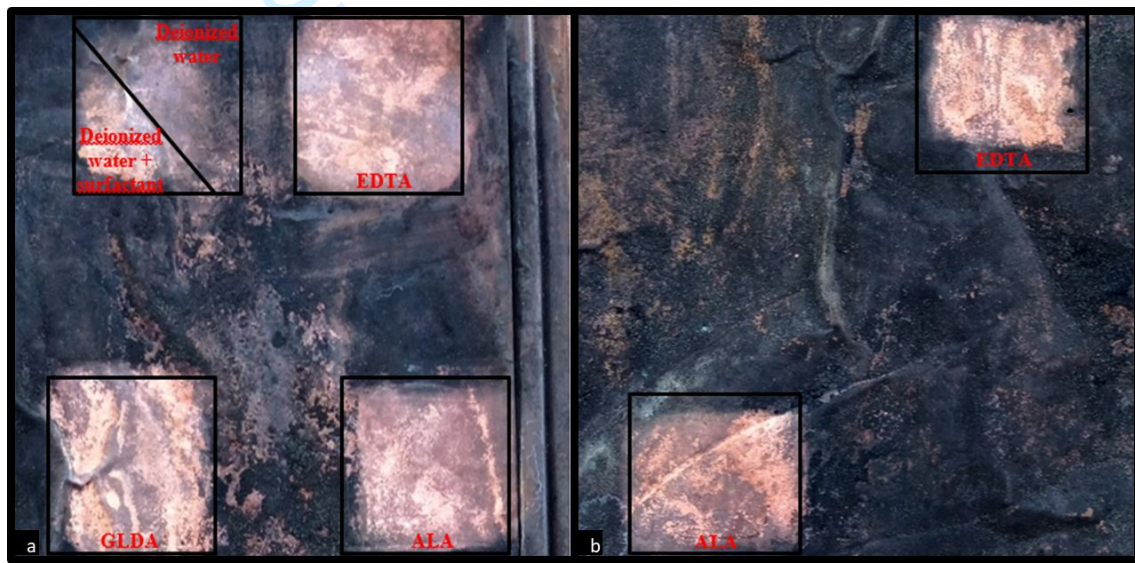


Figure S8. Cleaning tests on “Tramonto estivo” using deionized water (with and without surfactant), EDTANa₂/4, GLDA and alanine (a); cleaning tests on “Tramonto estivo” after washing the painting with deionized water using EDTA-Na₂/4 and alanine (b).