

## Research Article

# Analysis of the Quintilii's Villa Bronzes by Spectroscopy Techniques

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The aim of this work is the characterization, with different diagnostic tests, of three fragments of bronze artefacts recovered from the Villa of the Quintilii (located in the south of Rome). In particular, the sample alloys were investigated by different chemical and morphological analysis. Firstly, an analysis of the alloy, implemented through the electronic spectroscopy, was taken to discriminate the bronze morphology and its elemental composition. Subsequently, a surface analysis was realized by molecular spectroscopy to identify the alteration patinas on surfaces (such as bronze disease). Two diagnostic techniques are used for the alloy analysis: scanning electron microscopy (SEM) connected to the EDX spectroscopy (to study the morphology and alloy composition) and Auger electron spectroscopy (AES) (to identify the oxidation state of each element). Moreover, for the study of surface patinas, IR and Raman spectroscopies were implemented. All studies were performed on the "as received" samples, covered by a thin layer of excavated soil and on samples processed in an aqueous solution of sulphuric acid (10%), to remove patinas and alterations.

## 1. Introduction

The diagnostics of cultural heritage are based on physical methods and chemical-physical properties to obtain information on artefact chemical composition and their physical characteristics.

The aim of diagnostic tests is the study of artefact construction technique and execution, providing information about the original materials, their preservation state and on alteration products present on the artefact. Usually, the study of material surface is performed by different electron and/or photonic spectroscopies. The analysed object is "bombarded" with particles or electromagnetic radiation to obtain chemical and morphological information on the first monolayer or on the first surface layers (depth of few microns). The analysis of artefacts surface is important because it is the interface with the external environment and then it represents the border layer for the object (e.g., oxide film on a metallic material). Moreover, the surface may affect the aesthetic appearance and

can reveal the products of degradation (e.g., bronze disease). So, the surface characterization becomes crucial where the interaction phenomena with the external environment modify the artefacts. Moreover, the characterization of corroded layers is important to explain the causes of the degradation process.

Bronze patinas, in fact, are generally associated with the thin layer of products observed on ancient metals and alloys. They can result from corrosion due to exposure to atmospheric agents or to a prolonged burial in the soil (as in the case of the analysed artefacts).

Furthermore, alterations and patinas are strongly dependent on environments so that even external small changes can affect patina formation.

For all these reasons, the studies of patinas are very important to estimate factors in bronze stabilization.

The aim of this work is the detailed examination of alloy composition and corrosion and patinas of three Roman bronzes from Villa of the Quintilii excavation.

Historical “bronzes” are highly variable in composition; usually they contain a mixture of copper and tin as main components and traces of various elements as impurities (zinc, lead, nickel, iron, antimony, arsenic, and silver).

We focus our attention exclusively on copper and its deterioration mechanism, because this element is the main component of bronze disease.

The samples analysis was obtained by SEM microscopy, EDX (Energy Dispersive X-ray spectroscopy), AES (Auger electron spectroscopy), FT-IR (Infrared Fourier transform), and Raman spectroscopies. All the performed investigations were nondestructive and noninvasive and have been taken on as received and cleaned samples.

The cleaning process was obtained by sulphuric acid treatment ( $\text{H}_2\text{SO}_4$  aqueous solution 10%) for 10 minutes to dissolve copper carbonates.

## 2. Historical Background

The samples have been found in an archaeological excavation at the Villa of the Quintilii. This villa is located south of Rome and it is considered the largest and most luxurious suburban villa of the second century after Christ. The area covers 24 hectares and is rich in monumental remains. The name derives from Quintilii brothers, noble roman consuls, during 151 BC. The site is so large and the ruins so extended that in the past it was thought to even be a city to which, for this reason, was given the name “Old Rome” [1].

The fragments show a bad state of conservation, which is evident even by the naked eye: different processes of corrosion have caused material loss and chromatic alteration.

## 3. Instrumentation and Analysis

Using noninvasive and nondestructive techniques, the fragments have been studied by surface analysis investigations to provide information on the chemical composition of the material and its alterations.

Morphological analysis was performed by SEM and optical microscopies. Optical images of the sample were obtained by a zoom Stereomicroscope, model SZH Olympus, mounting objectives from 6x to 9x. The fragment dimensions range from 7 to 4 mm, with a thickness of about 3 mm (Figure 1).

SEM analysis was performed on both faces of our bronze fragments. The samples, being metal alloy fragments, have not been metallized.

Scanning electron microscopy (SEM) is a microscope that produces images of the samples by scanning them with a focused beam of electrons [2] and it allows for reaching a magnification of about 500,000x.

It consists of an electron gun, a column with a series of lenses to shape the electron beam, the sample chamber, and a series of pumps to keep the system under vacuum. When a sample is bombarded by an electron beam it produces secondary electrons (SE), back-scattered electrons (BSE), and characteristic X-rays. The produced electrons interact with atoms in the samples generating electronic signals, which

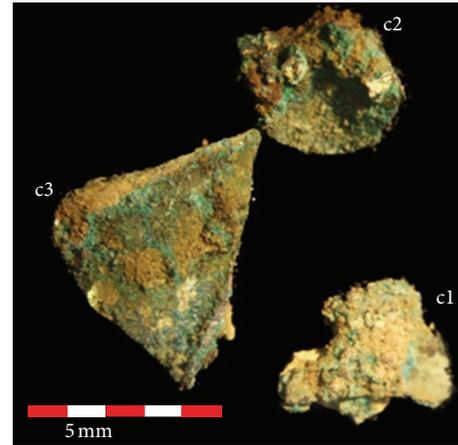


FIGURE 1: Bronzes taken into consideration in the analysis.

give us information about the sample’s chemical composition (BSE and characteristic X-rays) and the surface topography (SE) [3].

Scanning electron microscopy can show the sample superficial texture at nanometric level, revealing shape and dimensions of particles that constitute the surface layer; the qualitative and quantitative chemical analysis was performed in situ by energy dispersion X-ray (EDX).

The scanning electron microscope used for SEM analysis is a Field Emission Gun (FEG) Cold FEI Quanta 200F/Philips with an EDX microanalysis system with a crystal detector Si/Li, EDAX GENESIS 4000.

EDX analysis and SEM images have been obtained simultaneously with a 20 keV electron beam and a current of 200 pA (the best compromise for a good statistics in reasonable time and without saturate the detector EDX). Was chosen a magnification of 2500x (in most cases selecting a  $500\ \mu\text{m} \times 500\ \mu\text{m}$  frame) and integration time of 100 s. We acquired images using SEM microscope both in secondary electron mode (SE) and in back-scattered electron mode (BSE).

Chemical information was obtained also by Auger electron spectroscopy (AES). This analysis was performed in an ultrahigh vacuum (UHV) equipped for standard surface analysis with a pressure in the range of  $10^{-9}$  torr, bombarding the bronze artefact by a 2500 eV electron beam to a single incidence angle with respect to the normal sample surface. The electrons emitted as a result of the bombardment are detected by an electrostatic analyser (EA) fixed having acceptance to  $80^\circ$ .

AES is a spectroscopy used in the study of surfaces and gives chemical information on the first monolayers.

The Auger spectroscopy is not widely used in the field of cultural heritage, and in particular on bronzes. Indeed, since the middle of the 19th century, these materials have mostly been studied with “conventional” methods, such as optical microscopy, wet chemical analysis, atomic absorption spectrometry, and so forth, [4, 5].

This spectroscopy is based on the analysis of energetic electrons emitted from an excited atom after a series of

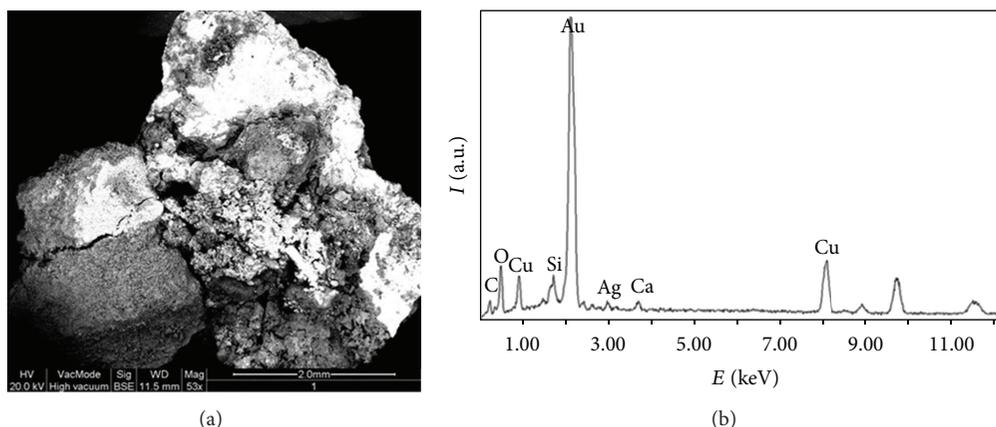


FIGURE 2: (a) BSE image of a bronze fragment and (b) bronze EDX spectrum.

internal relaxation events (Auger effect) [6] caused by an electron bombardment of sample surface.

To get the most useful information on degradation products and surface alteration and to discriminate the type of patina, we used two of the most accurate and sensitive molecular spectroscopic techniques; the Fourier Transform Infrared Spectroscopy (FT-IR) and Raman spectroscopy. FT-IR is a technique usually employed to obtain information about molecular structures, functional groups, and chemical compounds on sample [7]. The technique is based on the irradiation of sample surfaces with an electromagnetic radiation, which ranges between  $4000$  and  $400\text{ cm}^{-1}$  and then measuring the absorbed fraction to determine the vibrational transitions of the sample molecules [8]. The FT-IR is based on the possibility to realize a Fourier transform of emitted signals [9]. The used device is a 100 FT-IR Perkin-Elmer spectrometer.

Raman microscopy is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system [10]. It provides information on the atom vibrations in a crystal lattice studying the inelastic and Raman scattering of a monochromatic light (usually a laser in the visible range).

The laser light interacts with molecular vibrations, phonons, or other excitations in the system, and the produced shift in energy gives information about the vibrational modes in the system [11]. The Raman system in this work is a DXR Raman Microscope from Thermo Scientific.

#### 4. Discussion

EDX analysis (Figure 2(b)) for all “as received” samples (SEM images in Figure 2(a)) indicates the following as chemical composition: silver, aluminium, gold, calcium, chlorine, copper, iron, potassium, magnesium, phosphorus, and silicon.

Table 1 summarizes all elements’ percentage (excluding C) on the various areas of the samples subjected to EDX analysis.

Figure 3 shows the AES spectra for all elements on as received sample.

In the spectrum in Figure 3(a) we observe the Au line centred at  $69.80\text{ eV}$  (the detail of Au line is shown in Figure 4(b)) and the C ( $271\text{ eV}$ ) and O ( $503\text{ eV}$ ) lines [12, 13].

In Figure 3(c) we observe the characteristic lines of tin dioxide, respectively, at  $421.5$ ,  $425.5$ , and  $432.6\text{ eV}$  [14, 15] (Sn is one component in a bronze alloy) [13].

FT-IR spectrum in Figure 4(a) shows the malachite [ $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ ] characteristic bands. The FT-IR absorption spectrum of malachite shows bands at  $784$ ,  $818$ ,  $873$ ,  $1047$ ,  $1099$ ,  $1395$ ,  $1494$ ,  $3330$ , and  $3406\text{ cm}^{-1}$ . The band at  $3330\text{ cm}^{-1}$  is characteristic of stretching functional  $-\text{OH}$  group. The bands at  $1494$  and  $1395\text{ cm}^{-1}$  are characteristic of the stretching  $-\text{CO}_3$  group [16].

We see that in the  $\text{CO}_3$  group there is a double bond  $\text{C}=\text{O}$ . Probably the band at  $1635\text{ cm}^{-1}$  was due to stretching of the bond  $\text{C}=\text{O}$  [17]. The bands at  $873$ ,  $818$ ,  $777$ , and  $749\text{ cm}^{-1}$ , shown in Figure 4(b), represent the malachite fingerprint region. Instead, the band at  $1003\text{ cm}^{-1}$  is related to the asymmetrical stretching of the  $\text{Si}-\text{O}-\text{Si}$ .

The band at  $912\text{ cm}^{-1}$  is due to  $\text{Si}-\text{O}$  bond stretching [18].

The Raman analysis confirmed the FTIR results. In fact, the spectral pattern is typical of malachite (Figure 5); the spectrum shows peaks at  $177$ ,  $216$ , and  $267\text{ cm}^{-1}$ , which are related to  $\text{O}-\text{Cu}-\text{OH}$  bond bending. The mode at  $354\text{ cm}^{-1}$  is due to the  $\text{Cu}-\text{O}$  bending. Modes at  $432$  and  $533\text{ cm}^{-1}$  are related to the  $\text{Cu}-\text{O}$  stretching [16].

The modes at  $1060$  and  $3350\text{ cm}^{-1}$  are related to the  $\text{OH}$  bond-stretching, while those at  $1486$  and  $1087\text{ cm}^{-1}$  are related to the anion carbonate  $\text{CO}_3^{2-}$  stretching [19].

In a second spectrum taken from another region on the sample (Figure 6), it is possible to see the most intense bands at  $130$ ,  $188$ ,  $230$ ,  $351$ ,  $404$ , and  $984\text{ cm}^{-1}$ . These bands are characteristic of connellite  $\text{Cu}_{19}\text{Cl}_4(\text{SO}_4)(\text{OH})_{32}\cdot 3(\text{H}_2\text{O})$  [16]. The connellite is a copper chlorosulphate that is very rare in nature, which should turn to blue. It comes in the form of tufts of acicular crystals very delicate and is often associated with other secondary copper compounds, such as cuprite and

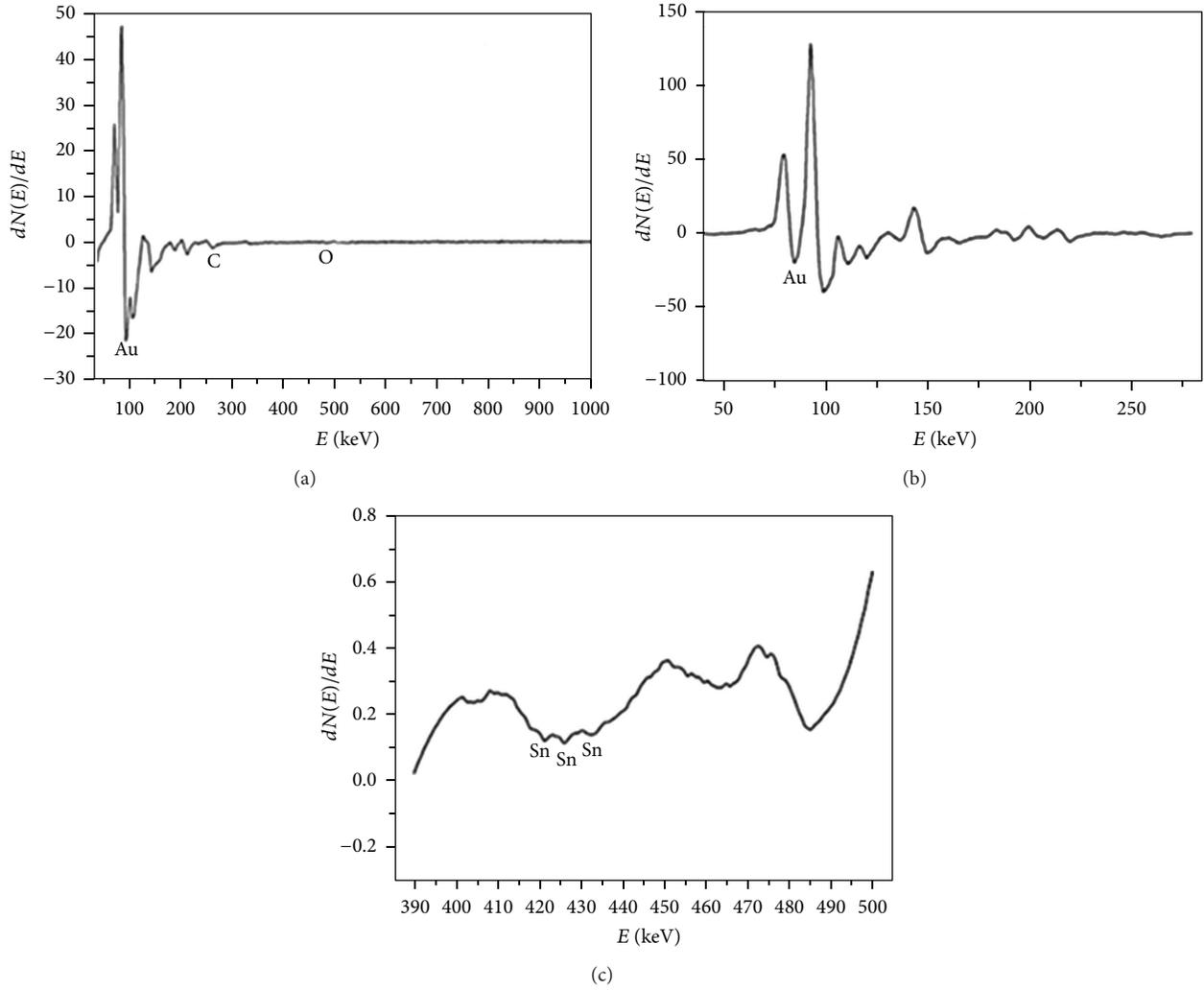


FIGURE 3: (a) Bronze Auger spectrum, (b) Au Auger spectrum, and (c) Sn Auger spectrum.

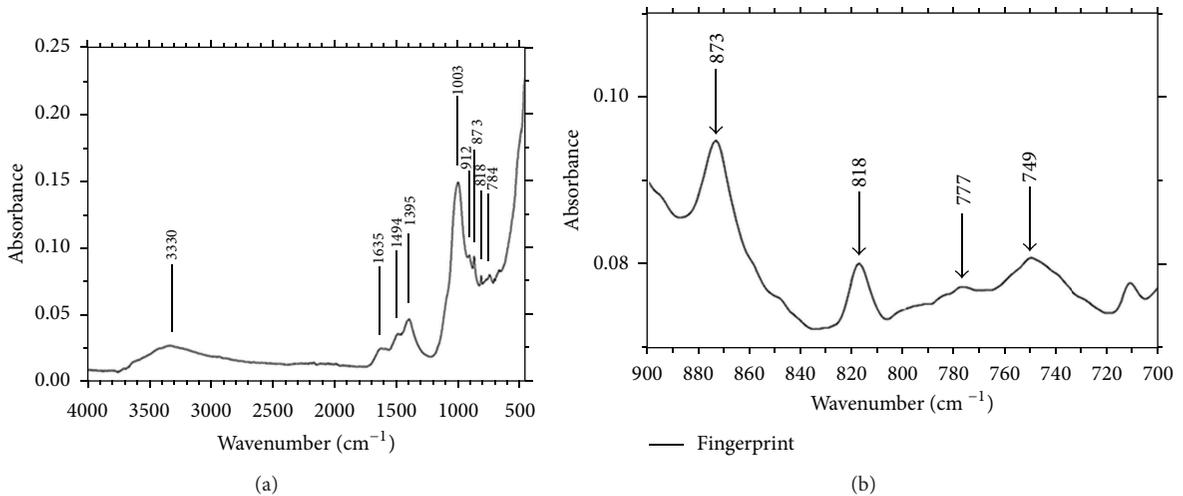


FIGURE 4: (a) Malachite FT-IR spectrum and (b) fingerprint region of malachite.

TABLE 1: Elements percentages in the sample for the different areas analysed.

	Ag	Au	O	Mg	Al	Cl	Si	P	K	Ca	Fe	Cu	tot
1 dx	—	—	53.69	0.91	7.26	—	12.60	1.56	0.66	7.61	1.96	13.75	100.00
1 sx	—	—	48.07	2.39	6.40	—	18.02	—	0.96	17.76	4.35	2.00	100.00
1 up	1.81	65.63	8.26	—	—	—	1.43	—	—	0.97	—	21.90	100.00
2 down	—	—	66.17	1.39	3.86	—	20.69	1.04	—	1.75	0.91	4.19	100.00
2 sx	—	—	56.66	—	3.15	—	16.59	1.50	—	1.75	1.14	19.21	100.00
2 up	1.72	57.28	13.69	—	0.32	3.63	1.02	—	—	0.36	—	21.98	100.00
3 rc	0.40	—	38.81	—	2.71	0.93	11.06	1.33	—	2.16	1.16	41.44	100.00
3 r	4.37	76.82	3.61	—	—	—	2.23	—	—	0.77	—	12.20	100.00

TABLE 2: Elements percentages in the sample c2 for the different zones analysed.

	Ag	Au	Ca	Cl	Cu	Fe	O	S	Si	tot
A	0.17	3.71	—	—	0.18	—	0.14	—	—	100.00
B	—	—	—	0.34	2.53	—	1.04	0.31	—	100.00
C	—	—	—	0.13	81.68	—	0.44	0.23	—	100.00
D	—	—	0.04	0.59	48.74	0.00	1.17	0.13	0.14	100.00

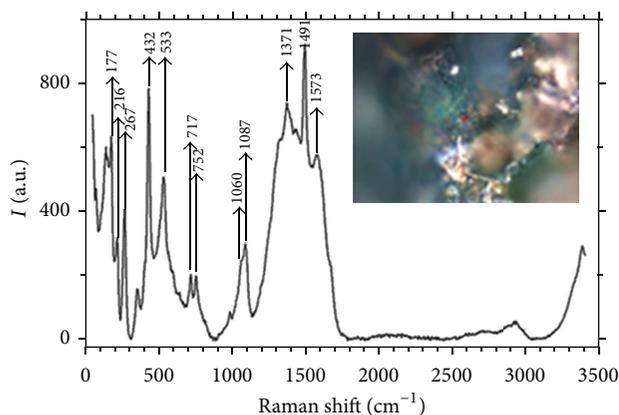


FIGURE 5: Malachite Raman spectrum.

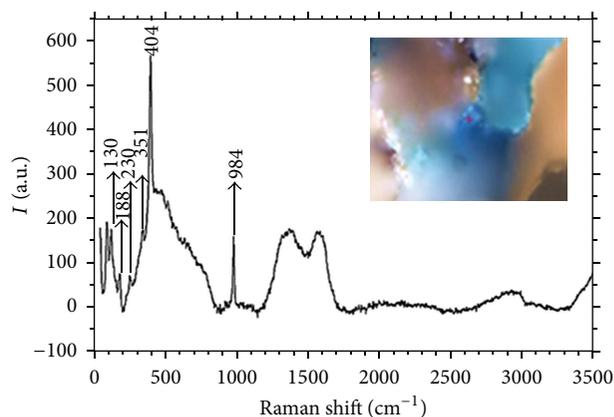


FIGURE 6: Connellite Raman spectrum.

malachite. Connellite can be classified as one of the bronze diseases.

The analysis on cleaned samples investigated the presence of gold on the alloy as suggested by the gilding visible, at necked eye, after patina removal (Figure 7).

From the SEM images of sample c3, in Figure 9, we observe that gold is distributed on the surface to form a thin film separated from the bronze alloy. The film thickness varies from about 200 nm to 400 nm. In effect, in the Roman era, major bronze statues generally underwent a gilding process with application of thin gold film on the artefact. Figure 8 shows the presence of cracks in the sample section caused by removal of carbonates (present in soil and in malachite) during acid treatment.

We can get more information about the sample's structure from the c2 cross section in Figure 8. There are four different structures, identified by the letters A, B, C, and D.

As shown in Table 2, the different structures have a different chemical composition. In addition, the gold covers

the entire alloy surface (A) with a small amount of Ag. On the gold coating (zone B), there is a patina formed predominantly of Cu, O, Cl, and S, while in the intermediate zone (C) the higher element is the copper with a small amount of O, S, and Cl which form a patina with a morphological structure clearly different with respect to other layers.

In the innermost zone, indicated with the letter D, the composition is predominantly similar to the B and C regions with contamination of Ca, Fe, and Si (the percentage values of all elements in all regions are given in Table 2).

The X-ray fluorescence analysis was conducted with a portable XRF model Artax 400 of Bruker and they were taken into different points of sample surfaces (as indicated in Figure 9).

## 5. Conclusion

In conclusion, we can remark that the used analytical techniques are very effective for a qualitative and quantitative

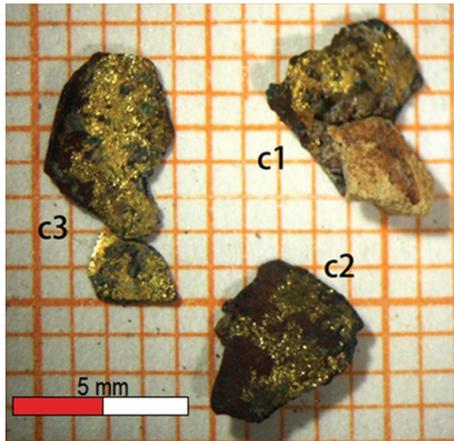


FIGURE 7: Bronzes after acid treatment.

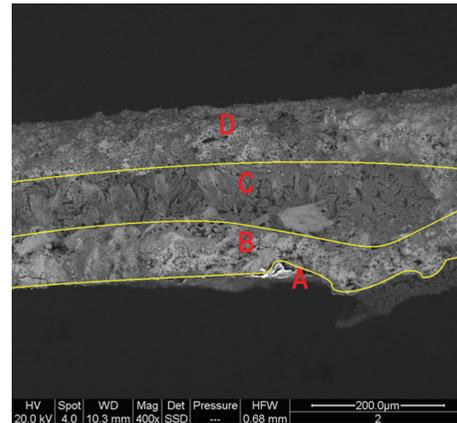


FIGURE 9: SEM image of bronze c2 cross section.

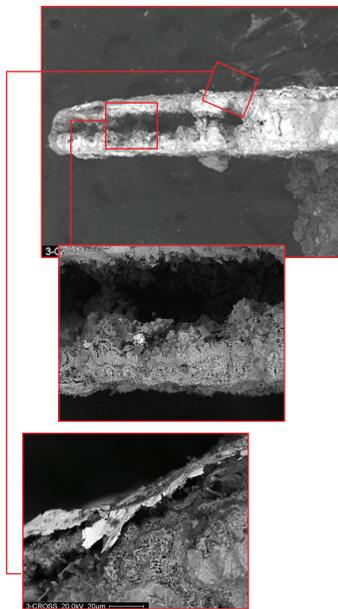


FIGURE 8: SEM image of bronze c3 cross section.

identification of the alloy composition and its alteration products. In fact, the investigation by SEM microscopy and AES and EDX spectroscopies allows us to identify the elemental composition of incrustated areas of “as received” samples revealing elements such as Cu, Sn, Si, Al, Ca, Fe, Mg, and P. The metal foil covering the samples (identifiable through the SE images and BSE) is formed by gold. Furthermore, from SE and BSE sample images (treated with  $H_2SO_4$ ) we have obtained the thickness of the gold foil, which has an average thickness of 300 nm. The artefacts appear to be composed of different layers. A first zone (A) is formed by a metal sheet that covers the alloy, consisting mostly of Au and a low percentage of Ag. An area below the gold sheet (B) is composed by alloy and its alteration products (chlorides, sulphides, and sulphates). An intermediate zone (C) is mainly formed by Cu, and finally an inner area (D) is composed of Cu, Cl, and S,

with the presence of some contaminants such as Fe, Ca, and Si.

Molecular spectroscopy FT-IR and Raman identified several alteration products from the study of patina mineral phases. In particular FT-IR spectroscopy indicates that the main surface alteration is the malachite  $[Cu_2(CO_3)(OH)_2]$  while Raman spectroscopy reveals in addition to malachite the existence of connellite  $[Cu_{19}Cl_{14}(SO_4)(OH)_{32} \cdot 3(H_2O)]$ , which is one of the products classified as bronze diseases.

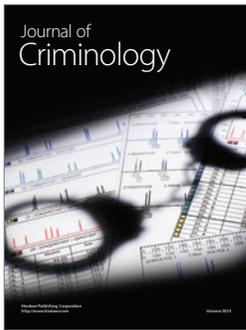
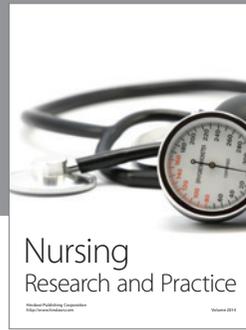
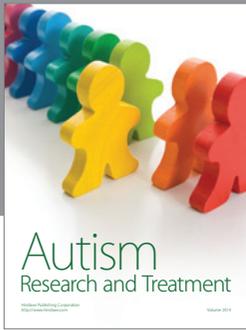
### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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