



# AN OVERVIEW OF ANALYTICAL TECHNIQUES AND METHODS FOR THE STUDY AND PRESERVATION OF ARTISTIC AND ARCHAEOLOGICAL BRONZES

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## ABSTRACT

The present review intends to give an overview on the type of information that is possible to gather from the application of different non-invasive and micro-destructive analytical techniques. Typically, methods that require the withdrawal of a sample, such as metallography, SEM-EDS, AAS, FTIR and Py-GC-MS are employed. Through their use, it is possible to identify the material constitution, to evaluate the degradation behaviour and the state of conservation of excavated bronze artefacts. It is also underlined how a non-invasive approach might be used whenever no sampling is allowed, though some limitation should be considered. Furthermore, analytical techniques play an important role in the characterisation and evaluation of the effectiveness of protective coatings and corrosion inhibitors before and after restoration procedures.

An interesting aspect is the implication of science for the recognition of forgeries, when analytical studies provide evidences able to prove or deny objects' authenticity.

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**KEYWORDS:** archaeological bronzes, metallography, corrosion, authentication

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## 1. INTRODUCTION

The study and understanding of manufacturing technologies and alteration phenomena of archaeological bronze artefacts is of great importance in the field of conservation and restoration of cultural heritage. In fact, they offer a "perspective of the past" through which a better understanding of ancient technologies is gathered. Also, they offer a "perspective of the future" allowing a better planning of intervention strategies aimed at avoiding, preventing and reducing degradation and deterioration processes.

In this context, a very important role is played by science, which provides the needed knowledge on physical-chemical aspect of works of art. Concerning bronzes, analytical investigations may be aimed at defining the composition of the alloy, characterizing the state of conservation, evaluating the performances of products and procedures used during restoration practices and obtaining information about the authenticity of the artefact (Mazzeo, 1993; Mazzeo *et al.*, 2001, Mazzeo *et al.* 2004).

## 2. CHARACTERIZATION OF THE ALLOYS

The elemental composition of a bronze alloy represents an important information to the archaeologist because it can provide a clue on the technology used for the production of the object and be a reference to its age and provenance. The characterization of the elemental composition of the alloy can be carried out using bulk or surface techniques. Advantages and drawbacks of the two approaches must be taken into account as they involve sampling in the first case, thus being invasive and destructive methods. On the contrary, a non-destructive (ND) approach allow to perform analysis directly *in situ* without requiring the withdrawal of a sample.

Concerning wet chemical and destructive methods, Atomic Absorption spectroscopy (AAS) is one of the most commonly used.

Despite the possibility to perform quantitative analysis with good sensitivity and reliability, it requires a rather high amounts of samples (50-100 mg) (Craddock, 1976).

Invasive and destructive methods allow reproducible and reliable results to be obtained, although they involve the complete loss of sample. In the field of Cultural Heritage, non-destructive techniques are preferred as they allow to keep the sample intact, and therefore to submit the sample to other complementary analytical techniques.

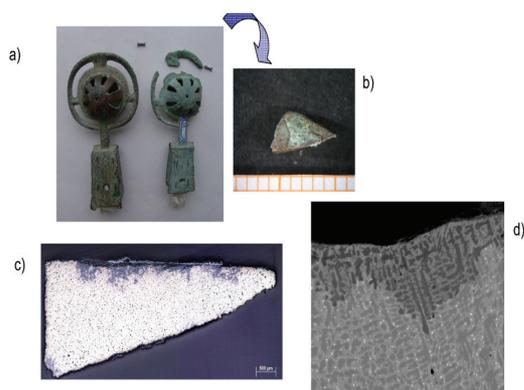
Among the non-destructive techniques, the portable X-ray fluorescence spectrometer (XRF) is a very attractive one, which allows to perform *in situ* analysis. This is often the choice when sampling is not permitted. The technique has the advantage of being portable and not destructive, but it doesn't allow to perform quantitative analysis and semi-quantitative results might be obtained if standards are used.

New insights into composition and structure of bronze sculptures has been successfully obtained by employing neutron imaging and neutron diffraction techniques (Van Langh *et al.* 2011). These are fascinating and innovative studies, which nonetheless require the availability of synchrotron facilities.

A typical approach consist in the preparation of a stratigraphic or metallographic section. However, metallography may be performed directly on-site through the use of a portable video microscope (Giardino *et al.*, 1996).

A metallographic section is prepared by polishing and etching the withdrawn micro-samples embedded in an epoxy resin. Optical microscope observations are of fundamental importance both to investigate the alloy microstructure and the type and extent of corrosion. Metallography allows, through etching with proper chemical solutions, to highlight phases and structures present in the alloy (Ammannati *et al.* 1991). Furthermore, SEM observation of metallo-

graphic sections provides not only a better definition of the surface morphology, but also information about composition in the case of using backscattered electrons (BSE) which is particularly useful when characterizing different phases (Figure 1).

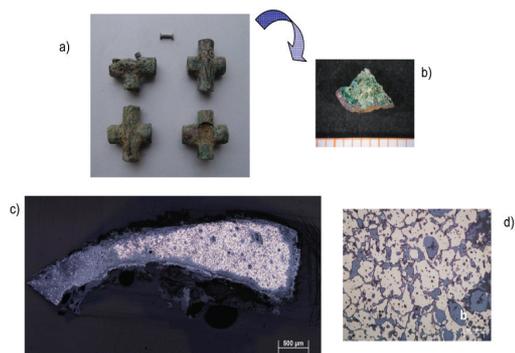


**Figure 1:** a) Chinese bronze bells recovered in the Liangdai archaeological site (Shaanxi province, China), b) stereomicroscope image of the withdrawn sample c) Optical microphotograph of the metallographic section (50X), d) BSE-SEM image where it is visible the dendritic structure and the preferential corrosion of the  $\alpha$ -phase (Cu-rich).

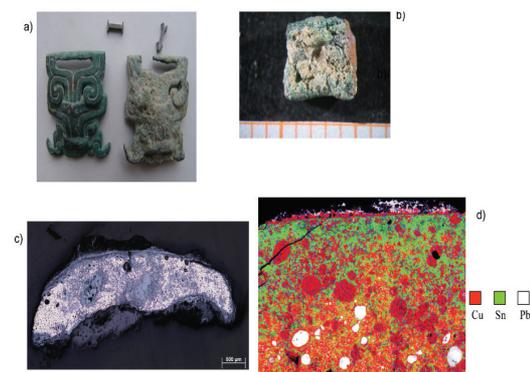
The morphological observation of metallographic section allows to obtain information about the manufacturing technology. Results obtained for samples excavated in the archaeological burial site in the village Liangdai (Shaanxi province, China) are reported. The optical and scanning electron microscopy allowed to put in evidence the presence of pure dendritic structure with coring, being the highest concentration of tin in the delta fringe surrounding the alpha-delta eutectoid (Figure 1).

A recrystallized grain structure was observed for one sample (Figure 2). The presence of a granular pattern and the absence of dendritic structure show that a thermal treatment has been performed after the cooling of the bronze melt.

Cored dendritic structures with lead and cuprite ( $\text{Cu}_2\text{O}$ ) globules (Figure 3). The dimension of inclusions is rather big, ranging from tenths to hundreds of microns. More-



**Figure 2:** a) Photo of tubular cross excavated from the Liangdai village archaeological site (Shaanxi province), b) Stereomicroscope image of the withdrawn sample, c) Optical microphotograph of the metallographic section (50X), d) detail of the recrystallized microstructure



**Figure 3:** a) Picture of harnesses excavated from the Liangdai village archaeological site (Shaanxi province), b) Stereomicroscope photograph of the withdrawn sample, c) Optical micrograph of the metallographic section (50X), d) EDX mapping which evidences a tin enrichment within superficial layers, lead globules within the bulk of the alloy and copper (or cuprite) globules in the external regions.

over, it seems that lead inclusions are partially corroded: this is a specific and peculiar feature that deserves more attention as uncommon corrosion mechanisms are involved.

Elemental analysis may be carried out by Energy Dispersive (EDS) or Wavelength Dispersive Spectrometer (WDS) coupled to the Scanning Electron Microscope (SEM) (Ammannati *et al.* 1991; Mello *et al.* 1983). In the case of samples from Liangdai, the characterisation of the alloy was, in some cases, a difficult task to achieve as many samples were deeply corroded, with few remaining uncorroded areas. For the most well-pre-

served metal samples it was possible to evaluate the composition by SEM-EDX. Variable and very high tin (12-22 wt.%) and lead (2-15 wt.%) contents of the bronzes are coherent with the archaeological and stylistic dating of the Western Zhou period (Gettens, 1969).

Promising results have been obtained in the analysis of the surface layers using the Auger spectroscopy and X-ray photoelectron (XPS or ESCA), which are very sensitive techniques for the detection of light elements (Mello *et al.* 1983).

### 3. CHARACTERIZATION OF THE STATE OF CONSERVATION

The characterization of the state of conservation includes the identification of corrosion products and deposits, and the extent of degradation within the alloy. The chemical characterization of corrosion products is very useful to better understand and investigate the interaction of the artefact and the environment (Mazzeo, 2005). For example, early detection of harmful chlorides is important in order to foresee an appropriate conservation plan.

The qualitative and quantitative characterisation of soluble components present in patinas of deterioration is of primary importance given that they are known to be dangerous. For this purpose, after determining the electrical conductivity (with a conductometer) of the rinsing water before, during and after the restoration operations (from which one can obtain a first estimate of the quantities of saline substances present), use is made of Ion Chromatography (IC) in particular for detecting anions (chlorides, sulphates, nitrates and oxalates) and cations removed by the rinsing water (Matteini *et al.* 1988), together with atomic absorption spectrometry (AAS) for metal cations (Matteini *et al.* 1991; Guida *et al.* 1994). As mentioned before, a current problem concerns the copper chlorides which are usually found in patinas of deteriora-

tion. It is known that they represent the ionic species which are mainly responsible for corrosion in copper and its alloys. The presence of these compounds in direct contact with bronze, together with the ability of chloride ions to set up centres of localised corrosion with highly penetrating properties (which appear on the surface in the form of small, pale-green craters) certainly represents the most worrying aspect in the conservation field since their elimination or their neutralisation is essential. Such an operation is very difficult because of the problem of locating the chlorides, and because the compositional analysis of the patinas, which does not always take samples from sufficient depth, often does not indicate their presence. In particular cases, cleaning operations on outdoor statues, such as the removal of gypsum black crusts, will enable such compounds to be detected. In particular, being the solubilisation and inhibition of copper hydroxy chlorides a time consuming operation, any lack of their location may create problems to conservator-restorers as it has consequences for the restoration budget planning. In fact only in cases of advanced deterioration, usually in a marine atmosphere, chlorides show themselves on the surface as greenish pitting formations. In other cases, these compounds are localised stratigraphically in direct contact with the metal surface, making their removal difficult.

The most commonly used method of removing salt from metal artifact is sodium sesquicarbonate. 0.1M of sodium sesquicarbonate solution is made by mixing  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ , and the artifact is submerged into the solution to elute chloride ion. Benzotriazole (B.T.A.) is used in rust prevention; it is typically used as a 3% solution by mixing with ethyl alcohol. On copper alloys, it reacts with copper to form films of Cu-BTA which prevents the surface to corrode

(<http://www.nrich.go.kr/eng/Science/Metal.jsp>).

The analysis of patinas and corrosion

products is carried out predominantly with spectroscopic techniques, such as molecular spectroscopy and microscopy (Infrared and Raman) (Matteini *et al.* 1991; Mazzeo *et al.* 2007; Mazzeo *et al.* 2005) while X-ray diffraction (XRD) is the chosen technique when the identification of crystalline phases is required.

The optical microscope observation of a cross section may be informative on the typology of corrosion occurred and thus revealing the object's biography until the recovery. In particular, the metallographic analysis allows to identify specific types of corrosion, such as the preferential enrichment in the outer layers of one of alloy components. This is a common phenomenon observed and reported for tin (Sn) in outdoor monumental bronzes (Bosi *et al.* 2002).

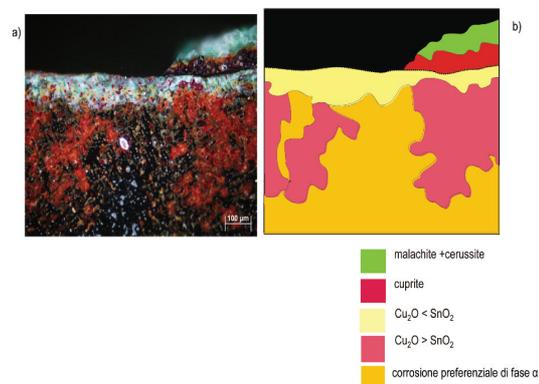
Electron microscopy coupled with energy dispersive electron microprobe (SEM-EDX) allows to perform a chemical analysis which provide the elemental information on a selected area. Molecular techniques, such as FTIR and Raman spectroscopy coupled to a microscope, not only allow the molecular identification of the corrosion products, but also their spatial location (Matteini *et al.* 1991; Mazzeo *et al.* 2007) within the stratigraphic structure.

As an example, figure 3 shows the cross section of a sample withdrawn from an archaeological bronze excavated in the archaeological site of Liangdai, Shaanxi province, China. This case study shows a bronze alloy with a high content of lead, which appears segregated in form of globules. These round-shaped formations are present both in corroded and non-corroded area of the alloy. Interestingly, in the corroded areas, they are transformed into cuprite probably due to a complex corrosion pathway involving redeposition of copper (Bosi *et al.* 2002).

Figure 4 shows the result of the molecular mapping aimed at studying the distribution of the corrosion products within the stratigraphy. The false colour map repre-

sents the result of an integrated analysis carried out in FTIR microscopy and elemental analysis (EDX).

Another important aspect, although not



**Figure 4:** a) Dark field microphotograph of the metallographic section (200X) reported in Figure 1. The sample has been withdrawn from a bronze bell excavated in the Liangdai archaeological site (Shaanxi province) b) Mapping the corrosion products

deeply investigated, is the characterization of the organic component of the natural patina of alteration, which may have a dual role of "binder" in the process of film formation of corrosion patinas and of precursors of given alteration reactions. The characterization of the organic substance can be performed using spectroscopic techniques, such as FTIR spectroscopy and microscopy or chromatographic ones such as Gas Chromatography-Mass Spectrometry gas chromatographic (GC-MS) and the Pyrolysis-Gas Chromatography / Mass Spectrometry (PY-GC-MS) (Chiavari *et al.* 1999; Mazzeo *et al.* 1989).

#### 4. EVALUATION OF MATERIALS FOR CONSERVATION AND RESTORATION

In the context of assessing behaviours and performances of protective coatings and corrosion inhibitors, several chemical and electrochemical techniques can be employed.

Typically, tests are performed on standard specimens and in isolated or confined areas of the works of art to be restored. The protectives of interest are applied, charac-

terized and their performance is monitored over time after exposure to natural or artificial aging conditions.

They are evaluated in terms of:

- Inhibition and protective properties: electrochemical impedance spectroscopy is commonly used, even *in situ*;

- Colour change: for aesthetic reasons, the patina, after treatment, should keep as much as possible the colour unchanged. For this purpose, techniques such as colorimetry are used to evaluate the phenomena of yellowing or whitening of the protective coatings. A change in colour is also a mean to evaluate the stability of the treatment against exposure to accelerated ageing (varying RH, T and UV exposure);

- Chemical inertia: analytical techniques such as FTIR spectroscopy or gas chromatography-mass spectrometry allow to verify the composition of the protective coating in time and if it causes undesired reactions with the substrate;

- In-depth penetration: FTIR microscopy is successfully used to obtain a mapping of the product within the stratigraphic section in order to assess its degree of penetration.

It should also be noted that the effectiveness of a treatment is closely related to composition of products of degradation and the type of corrosion in place and therefore the analytical protocols for the study of the performance of new protection products should take into account the characteristics of the coating and the environment of exposure.

Currently, for the conservation of outdoor bronzes protective coatings are applied regardless the nature and composition of the patina. Acrylic resins (Incralac), some types of waxes (wax R21, TeCe Wachs 3534F) and organic corrosion inhibitors (BTA, benzotriazole) are broadly used. The waxes can be applied directly on bronze or above a pre-existing layer of acrylic resin. In the latter system, known as the method of the *double layer*, the wax acts as a sacrificial layer (Marabelli *et al.*, 1991; Letardi, 2004;

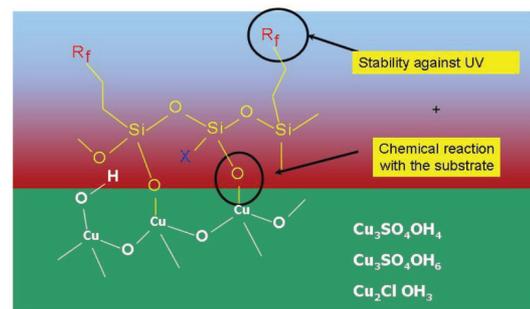
Joseph *et al.* 2007).

As an example, the results of an experimental study conducted in our laboratory are reported. The aim was to test, depending on the type and composition of the corrosion patina, innovative products for protection and corrosion inhibition of outdoor bronzes. They are listed in Table 1:

**Table 1: Description of tested protectives and corrosion inhibitors**

Treatment (T) Inhibition (I)	Commercial name	Tipology
T1S	Dynasylan F8263	organic-inorganic
T2S	Dynasylan SIVO clear K1/K2	organic-inorganic
T3S	Cuprite layer	Inorganic
T reference	Incralac	Organic
I1S	Limewater 0,5%	Passivation
I reference	Benzotriazole	Complex

For the discussion, particular attention will be given to the results obtained for T1s and T2S treatments. The nature of the selected product is organ - silane and they are normally employed for the consolidation of stone materials because of their ability to form chemical bonds with the Si-OH groups present in these substrates. The aim of the research was to test the performances in terms of protection and inhibition when applied on a patina of corrosion of different composition. In particular, tests were aimed at verifying the formation of bonds Si-O-Cu with the OH groups of copper hydroxy sulphates and / or copper hydroxy chlorides



**Figure 5: Interaction of silanes with hydroxyl groups of bronze corrosion products**

(brochantite, antlerite, atacamite) (Figure 5) (Letardi, 2004).

The treatments were applied, until saturation, on different types of samples in particular:

- urban natural (UN): copper plates exposed 80 years to the urban atmosphere of Monaco;

- urban artificial (UA): bronze sheets (85% copper, 5% tin, 5% lead and 5% zinc) upon which a brochantite patina was artificially produced (Pichler method);

- marine natural (MN): bronze sheets (85% copper, 5% tin, 5% lead and 5% zinc) 1 year exposed to the marine environment of Cabo Raso (Portugal).

Before the application of the different products, the corrosion layers were characterized in terms of thickness (Eddy currents) and roughness measurements, colorimetric analysis, FTIR microscopy analysis, electrochemical impedance spectroscopy and XRD (Table 2).

**Table 2: Description of the composition of the patinas**

Sample	Patina composition
UA	Antlerite with traces of brochantite
UN	Brochantite
MN	Atacamite, traces of phosphates, silicates, malachite, calcium oxalate

At the end of this characterization, the treatment was carried out and, subsequently, aging in natural and artificial environment was performed on two separate series of samples. For this purpose, the MN samples were exposed for 18 months in Cabo Raso and in Genoa. A series of samples UA and UN have been exposed to Genoa for 18 months and another one has been artificially aged according the following protocol:

(I) exposure to UV radiation (standard

method EN ISO 11341) (2004);

(II) exposure to a saline solution consisting of NaCl (0.5 g/L) + (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (3.5 g/L) (standard method ISO 9227) (2006).

The samples were exposed to radiation and to the salt solution alternately to two weeks until the achievement of 2000 h of artificial aging.

The samples were monitored over time through visual observations, colour measurements, thickness measurements and electrochemical impedance spectroscopy after 6, 12 and 18 months. The colour differences on copper roof samples were measured by conventional methods<sup>1</sup> before and after exposure.

Concerning the treatments, a\* (red-green components) and b\* (yellow-blue components) values doesn't show modification after fluorosilane application. By contrast, the  $\Delta L^*$  value (lightness) decrease significantly and lead to high  $\Delta E^*$  values (colour difference). After artificial weathering a\* and b\* values increase in yellow composition, and  $\Delta L^*$  values decrease. It can be notice a slightly difference in colour before and after ageing. This feature result in a whitish and milking appearance of the surface, previously noted by Brostoff (Brostoff, 2003).

Regarding the natural patina as a reference, significant modification are evident after artificial weathering. Probably due to a corrosion process, a\* and b\* values move to more green areas and  $\Delta L^*$  decrease dramatically. A visual appearance show green stripes on coupons edge and green areas after artificial weathering.

The obtained results demonstrate the effectiveness of the two silanes both as protective coating and as inhibitors when compared with the reference methods (Table 1). In particular it was observed that both the Incralac and the benzotriazole very quickly loose the protective and inhibition properties after exposure, while the two silanes show a more stable behaviour over time. The electrochemical impedance spectroscopy (EIS) analysis has clearly shown that the perform-

ance of protective systems and inhibition, vary depending on the nature of the patina and environmental exposure, thus demonstrating the need to develop standard protocols for the evaluation of their performances, which should take into account the above mentioned aspects.

## 5. A CONTRIBUTION TO AUTHENTICATION STUDIES

The recognition of forgeries are frequently based on studies of iconography and the use of advanced physical methods of investigation, such as X-rays radiography. However, in some cases, both methods are not exhaustive due to the fact that from the technological point of view, modern production methods are not dissimilar from those used in antiquity and may be replicated.

The elemental composition of the alloy is occasionally used as a reference for a primary and generic historical position of the artefact, such as it happens for the post imperial Chinese bronzes characterized by high percentages of lead in place of tin.

It is still cause of strong debates, the question relating to the possibility that dating bronzes from different historical periods can be carried out by different average percentages of the constituent elements (copper, tin and lead). As an example, numerous archaeological studies are already available concerning Chinese bronzes and the determination of alloy compositions within the Erlitou (3500-2500 B.C.), Shang (II millennium B.C.) and Western Zhou (XI century - 771 B.C.). However, analytical results show that it is generally difficult to make direct relationships between elemental composition and historical period.

The characterization of the alloy should be always coupled to the analysis of patina, which, especially for archaeological bronzes, show peculiar morphology and composition, and can hardly be falsified.

Depending on the environment of exposure (underground, atmospheric, marine)

bronze alloys form different corrosion products such as hydrated copper carbonates, sulphates, chlorides, oxides as well as those resulting from other alloying elements, such as tin and lead.

The presence of strange or anomalous compounds may be an indicator of falsification. For example, natural or artificial pigments have been widely used for the counterfeiting of patinas. Among them we recall natural pigments, malachite and azurite, and artificial ones such as emerald green [ $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$ ], a copper-based acetate arsenate industrially produced in Germany in 1814, Prussian blue ( $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ ), marketed in Europe since the early 18<sup>th</sup> century, the artificial ultramarine ( $3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{Na}_2\text{S}$ ) produced in the first half of the 19<sup>th</sup> century and smalt ( $\text{CoO} \cdot n\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{K}_2\text{O}$ ), a blue pigment of vitreous nature used both East and West since the Middle Ages. As pigments, their application on the metal surfaces must necessarily involve the use of organic binders, which are generally of proteinaceous nature (animal glues and/or vegetable gums).

It should be noted that the identification of common corrosion products may not always be straightforward for the authentication of an object. In fact, corrosion products detected on bronzes can be easily chemically reproduced (Hughes *et al.* 1991).

However, concerning archaeological bronzes, the stratigraphic succession of corrosion products formed by the interaction between the constituents of the alloy and the subsoil during the long period of burying (Robbiola, 2006) can be straightforward for authentication studies. Long-term processes are hardly reproducible in laboratory experiments and the modern analytical techniques, such as FTIR microscopy, allow not only to characterize but also to precisely localize the corrosion products within the sample's cross section (Mazzeo *et al.* 2004, Mazzeo *et al.* 2007). Figure 6 shows the results of analyses carried out by  $\mu\text{ATR-FTIR}$  directly on the stratigraphic section of

a sample taken from a bronze horse purchased on the antiques' market in China (fig. 6). The complex investigation has led to the conclusion that the patina of corrosion has been produced artificially. The section is composed of a first layer of coarse white colour brown in direct contact with the metal alloy, above which there are two layers of green colour containing particles also white in colour. The stratigraphy also shows the presence of a thin layer of black/red colour located at the interface of the two layers green.

It has not been possible to characterize the nature of this layer, probably consisting of cuprite ( $\text{Cu}_2\text{O}$ ), which is inactive in the selected infrared range ( $4000\text{-}650\text{ cm}^{-1}$ ). The layer of coarse preparation consists of smithsonite, yellow ochre and binder of probable proteinaceous nature, while the overlying layers are green be composed of green earth (probable glauconite:  $(\text{K}, \text{Na})(\text{Fe}, \text{Al}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$ ).

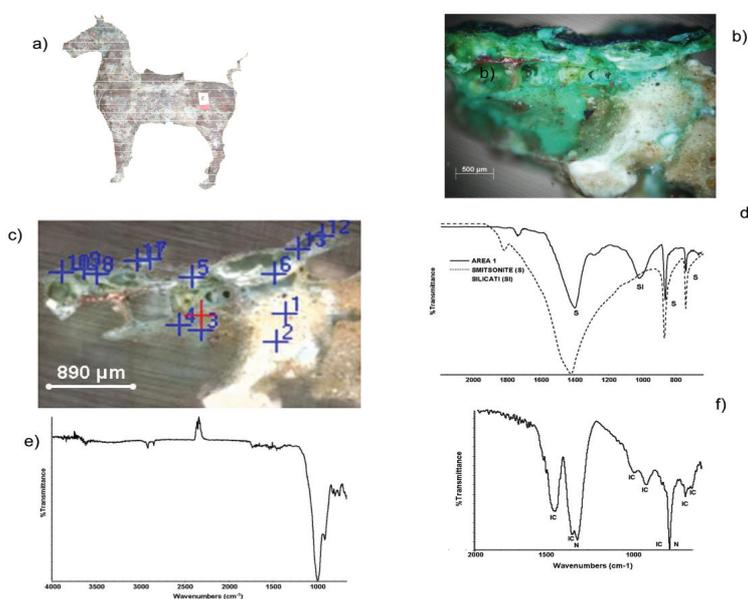
## CONCLUSIONS

As concluding remarks it can be said that the presented work has provided an interesting insight into recent application of analytical techniques for the characterization of archaeological bronzes. It is relevant un-

derlining that the best approach involves the use of both non-invasive and micro-destructive techniques, based on a well-defined analytical strategy. The focal point would be to obtain as much information as possible from the least invasive action.

Attention has been focused on innovative protective coating, to stress out the need to well study and precisely characterize their mechanism of action. The effectiveness of silanes, demonstrated through the use of EIS, is relevant due to its easiness of application and the improved durability of the treatment. It is worth underlining the importance of developing and implementing analytical protocols aimed at testing treatment efficiency.

A last, but not least, issue is the one which concerns authenticity. This is particularly important when museum exposition and value quantification are concerned. It has been pointed out that aesthetical and iconographical considerations cannot be conclusive and should be always accompanied by scientific investigations, even though the access to analytical techniques can be often restricted and expensive. Moreover, even the scientific response has to interpreted consciously.



**Figure 6:** a) Bronze Chinese horse b) microphotograph of sample's cross section c)  $\mu$ -ATR analysis points d) ATR spectrum ( $2000\text{-}650\text{ cm}^{-1}$ ) showing bands of smithsonite and silicates e) ATR spectrum ( $2000\text{-}650\text{ cm}^{-1}$ ) showing bands of yellow ochre and traces of proteic substances f) ATR spectrum ( $2000\text{-}650\text{ cm}^{-1}$ ) showing bands of hydroxycarbonates (IC) and nitrates (N).

## FOOTNOTE

1. The colorimetric data have been carried out using CIEL\*a\*b\* colour space where L\* is lightness, a\* is the red –green component and b\* is the yellow-blue component. The colour differences ( $\Delta E^*$ ) after treatment and after exposure were calculated according to differences of its single component  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  using the following equation:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

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