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Combined elemental and microstructural analysis of genuine and fake copper-alloy coins*

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Abstract. **Innovative noninvasive material analysis techniques are applied to determine archaeometallurgical characteristics of copper-alloy coins from Florence's National Museum of Archaeology. Three supposedly authentic Roman coins and three hypothetically fraudolent imitations are thoroughly investigated using laser-induced plasma spectroscopy and time of flight neutron diffraction along with 3D videomicroscopy and electron microscopy. Material analyses are aimed at collecting data allowing for objective discrimination between genuine Roman productions and late fakes. The results show the mentioned techniques provide quantitative compositional and textural data, which are strictly related to the manufacturing processes and aging of copper alloys.**

Keywords: *laser-induced plasma spectroscopy, neutron diffraction, archaeometallurgy, copper alloy.*

1. Introduction

Compositional and microstructural analyses of archaeological copper-alloy artefacts provide information about ancient manufacturing processes and aging of ornamental and utilitarian metallurgical products of the past. Innovative noninvasive techniques that exclude the unacceptable damage of the sample offer reliable and practicable ways to perform archaeometallurgical investigations, which are gradually replacing traditional approaches based on material sampling. Noninvasive techniques can also extend the investigation to the whole artefact, which plays an important role in this substantial evolution of the material characterisation in the field of cultural heritage.

Microdestructive and nondestructive techniques are of particular interest for studying such small objects as, for example, coins, statuettes, jewels, etc. Among them, laser-induced plasma spectroscopy (LIPS) and time of flight neutron diffraction (TOF-ND) represent two complementary approaches, which allow achieving quantitative surface and bulk data, respectively.

LIPS is a microanalytical elemental technique (typical ablation spot smaller than 100 μm) whose invasiveness is negligible in most cases [1]. The measurement procedure is relatively simple and fast and does not need any sample preparation. It has been proposed as a versatile analytical tool for characterising pigments, metal alloys, glasses, and ceramics [2, 3]. The application of LIPS for investigating ancient copper-alloy artefacts appears to be the only technique, which makes it possible to measure surface enrichments and depletions of alloying metals [4]. Alternative techniques such as scanning electron microscopy coupled with energy dispersive X-ray (SEM/EDX) spectroscopy and particle induced X-ray emission (PIXE) involve a very low penetration, while X-ray fluorescence (XRF) does not provide any depth resolution. Quantitative elemental depth profiles, which can be achieved using LIPS represent indeed the best solution for archeometallurgical studies of copper-alloy artefacts [4, 5].

TOF-ND is a nondestructive analytical technique, which exploits the deep penetration of thermal neutrons. It provides reliable bulk compositional and microstructural data averaged over large measurement volumes (up to several cubic centimetres). Its use is particularly interesting whenever dealing with artefacts crafted through hardening and annealing treatments since the refinement of diffraction patterns and the reconstruction of pole figures make it possible to derive information about the manufacturing processes.

TOF-ND was first proposed for the characterisation of metal archaeological objects in 2002 [6] and since then many works confirmed the reliability of the technique for quantitative multiphase, texture and residual stress analyses [7 – 9] TOF-ND was moreover employed in authentication studies based on compositional comparisons [10] and to discriminate between struck and cast coins [11, 12]. This approach, anyway, still has to be applied widely in the authentication practice.

In the present work the above mentioned techniques, along with 3D videomicroscopy and environment scanning electron microscope (ESEM) were tested in order to evaluate their potential for approaching coin authenticity problems. Three genuine and three fake copper-alloys coins from Florence's National Museum of Archaeology were preliminarily classified on the basis of numismatic criteria. Then they were thoroughly investigated from compositional, microstuctural, and morphological standpoints in order to assess the possibility of achieving objective discrimination criteria between genuine productions of Roman mints and counterfeits.

2. Materials and methods

A set of six coin investigated is shown in Fig. 1. They were selected from the Medici-Lorraine Roman collections of Florence's National Museum of Archaeology, which are of unknown provenience. The examination of the iconography

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Figure 1. Recto and verso of the coins under investigation.

and inscriptions led a numismatic expert to classify the coins as sesterti of the emperor Nero (54–68 AD). In addition, their weight (ranging between 20–31 g) was compatible with Nero's coinage, which is usually referred around 25 g.

According to visual and tactile examinations of the contours, sharpness of the inscriptions and other morphological features $C_{I–III}$ were assumed to be genuine, and $C_{1–3}$ to be replicas crafted along the last five centuries. This historical and empirical authentication conclusion pointed out from the numismatic standpoint represents the starting point of the present study, which was aimed at achieving any congruence or discrepancy with such preliminary authentication in terms of material analyses.

Alloy compositions of the six coins were measured using LIPS while TOF-ND was used to achieve phase and texture characterisation of the supposedly fake coins ($C_{1–3}$). Furthermore, 3D videomicroscopy inspections and some ESEM examinations were also carried out in order to point out any possible tool mark to be associated with the manufacturing processes. Thus in particular, we explored the potential of these techniques in order to discriminate between cast and struck coins.

LIPS measurements were carried out using a homemade portable device equipped with a compact electro-optically *Q*-switched Nd : YAG laser (1064 nm) and four compact Czerny–Turner spectrometers (AvaSpec-2048 FT, Avantes) with CCD linear arrays detectors covering the spectral range 200–630 nm with a resolution of 0.06 nm. A detailed description of the instrument as well as of its calibration and accuracy for quantitative analyses of binary, ternary, and quaternary copper alloys (Cu, Sn, Zn, Pb) can be found elsewhere [4].

Quantitative chemical analysis of each coin was derived through the measurements of elemental depth profiles over some thousands of laser shots. According to the typical behaviour, after an initial fluctuation of the elemental content, depending on corrosion phenomena or on the presence of coatings, the depth profile gradually approaches an almost stable value, which represents the bulk composition [4, 5].

TOF-ND measurements of the three supposedly fake coins were carried out on INES (Italian Neutron Station at ISIS, Rutherford Appleton Laboratory, UK) [13, 14]. Diffraction patterns measured were analysed using multibank Rietveld refinement via the GSAS (general structure analysis system) code [15] in order to derive quantitative multiphase characterisation. Furthermore, reconstructed pole figures were calculated through a number of measurements carried out using an Eulerian goniometer and data elaboration using the MAUD (material analysis using diffraction) code [16]. Further details on the TOF-ND techniques can be found in the literature cited.

Finally, 3D inspections of the coin surfaces along with electron microscopy examinations were carried out using a homemade videomicroscope and a commercial ESEM system, respectively. 3D videomicroscope was equipped with a moving optical head including an objective and a CCD camera, which made it possible to reconstruct the 3D model of the surface under examination through the so-called 'shape from focusing' technique [17]. The field of view of the instrument was 5×5 mm while its vertical resolution was around 10 µm.

3. Results

From two to four elemental LIPS depth profiles were measured in different zones of each coin. The coins $C_{I–III}$ and C_1 resulted to be composed of pure binary brass (Cu–Zn), whereas $C_{2,3}$ were quaternary (Cu–Zn–Sn–Pb) and ternary (Cu–Zn–Pb) alloys, respectively. Compositional variations up to a factor 5 were observed for the coins $C_{I–III}$ and C_1, whereas the profiles of $C_{2,3}$ were relatively stable. Some representative examples of Zn-depth profiles are displayed in Fig. 2. One can see from the figure a significant surface depletion (dezincification) for the coins C_{III} and C_1, whereas C_2 exhibits only a moderate variation around about 9.5 wt%. In all the cases, after several hundreds of laser shots the Zn content gets almost constant around what can be assumed to be the bulk composition.

Quantifications of the alloying metals in the bulk were achieved from depth profiles of Fig. 2 and from other similar saturating profiles measured for the other coins by averaging the Zn, Sn, and Pb contents measured over the last hundreds of laser pulses. The results listed in Tab. 1 show that similar compositions, with a Zn content between 17–19 wt%, were found for the coins $C_{I–III}$ and C_1, whereas those of $C_{2,3}$ were decidedly different.

Phase analyses of the coins $C_{1–3}$ were derived through Rietveld refinements of the corresponding neutron diffraction patterns. The phases matched were α(Cu), Pb, and cuprite (Cu_2O). For binary copper alloys the calculated lattice parameter of α(Cu) phase allows deriving the content of the alloying metal using suitable calibration curves relating lattice param-

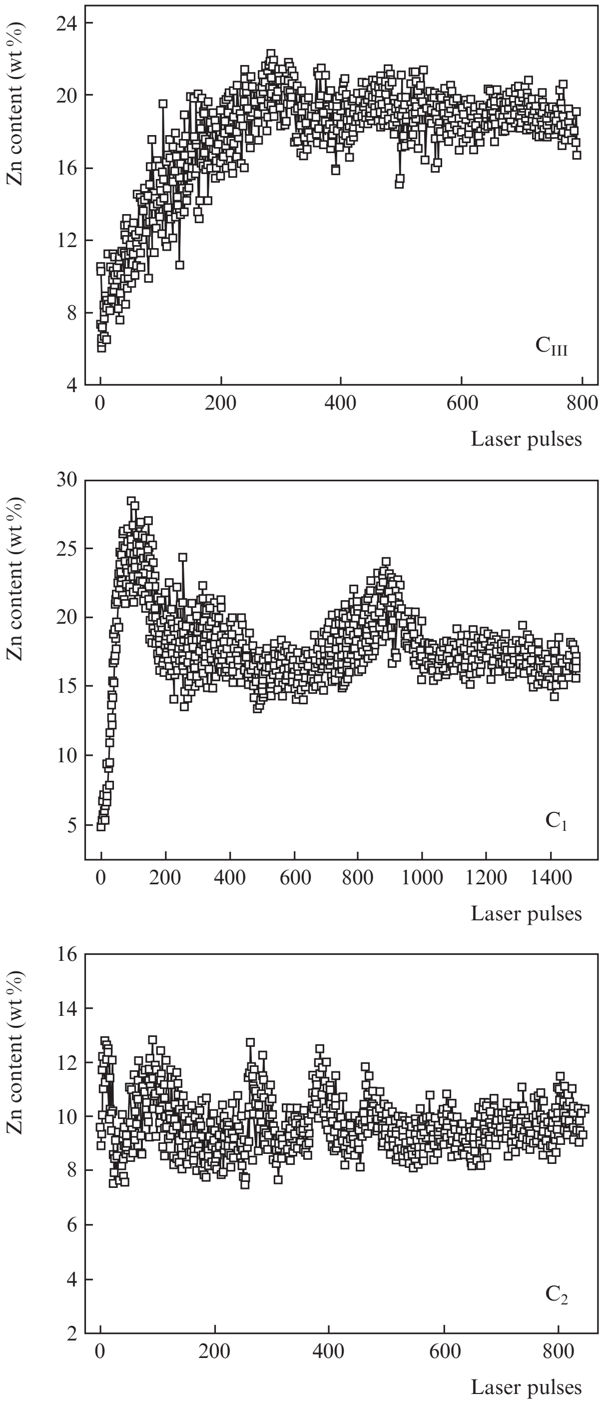

Figure 2. LIPS Zn depth profiles of the coins C_{III}, C_1 and C_2.

eter of the face-centred cubic (fcc) structure to the degree of alloying [7, 14]. The same can be extended to leaded binary alloys (usually named ternary alloys) since Pb segregates as an independent phase during the solidification of the metal, i.e. it is immiscible in the solid phase. Conversely, TOF-ND cannot be calibrated for quaternary alloys (Cu–Sn–Zn–Pb) since there are no ways to separate the contributions of Zn and Sn to the lattice parameter.

Table 1. Alloy compositions of the coins as derived from the LIPS elemental depth profiles.

Sample	Zn (wt %)	Pb (wt %)	Sn (wt %)
Coin C_I	17.5 ± 1.1	–	–
Coin C_{II}	17.4 ± 0.9	–	–
Coin C_{III}	18.9 ± 0.9	–	–
Coin C_1	17.1 ± 1.0	–	–
Coin C_2	9.5 ± 0.7	3.0 ± 0.4	3.1 ± 0.3
Coin C_3	13.7 ± 0.6	1.1 ± 0.3	–

Table 2. Phase and elemental composition of C_{1-3} as derived from Rietveld refinements of TOF-ND patterns.

Sample	*a* (Å)	Cu (wt %)	Zn (wt %)	Pb (wt %)	Cu_2O (wt %)
Coin C_1	3.656	81.1	18.2	–	1.2
Coin C_2	3.651	Cu-alloy 97.4 wt%		2.6	–
Coin C_3	3.647	85.3	14.7	0.7	–

The comparison between LIPS (Table 1) and TOF-ND (Table 2) elemental results for the coins C_{1-3} show very good agreement. Weight percentage values can be considered practically coincident whether taking into account the experimental errors of LIPS and the typical sensitivity of TOF-ND, which is around 0.5 wt% [7, 14]. It can be easily demonstrated that the congruence of the data is extended to the quaternary alloy of the coin C_2 too whether comparing the lattice parameter corresponding to the LIPS data. This is a cross-assessment of these two innovative analytical techniques.

Besides alloy composition information, TOF-ND also allows quantifying mineral content and the presence of statistically preferred orientations of crystallites (texture). As it can be seen in Table 2, only C_1 had a relevant copper oxide (cuprite) content, which is a clue of long-time aging in humid environment.

Reconstructed pole figures of the supposedly fake coins (C_{1-3}) are displayed in Fig. 3. The coin C_1 exhibited a (100) fibre parallel to the normal direction of the coin, which represents the typical texture component for uniaxial compression of the fcc lattice. This provides evidence the coin was struck by compression between two dies. A weak (100) fibre texture was also pointed out for the coin C_3, whereas C_2 presented a weak cube texture. This latter feature allows ruling out that the coin underwent a striking process; it was more likely cast

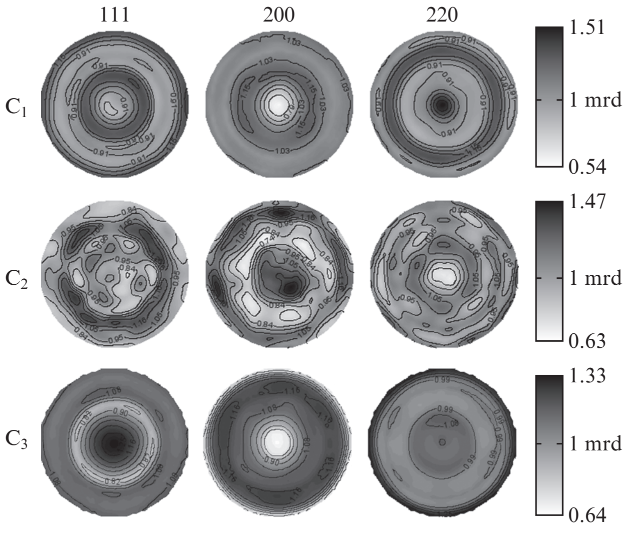

Figure 3. Reconstructed pole figures of the coins C_{1-3} (mrd is the multiple of random distributions).

in a mould. Actually, cube texture is typically formed during the solidification of planar-geometry objects.

The inscriptions of all the coins were inspected through 3D videomicroscopy and ESEM in order to point out morphological features, which could be associated with the striking process. Well-readable 3D microrelieves were achieved for the coins C_I, C_{III}, C_1, and C_3, whereas C_{II} presented encrustations, which disguised the edges of the letters. Figure 4 displays screenshot of letters 'A' and 'M' of the coins C_1 and C_2. The former was rather smooth and presented multiples edges whereas the latter exhibited straight profiles and it was single edged.

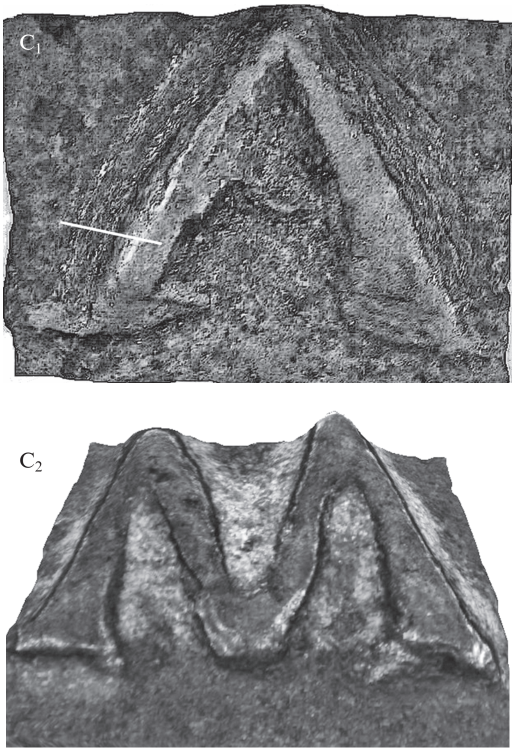

Figure 4. 3D relieves of two letters on the coins C_1 and C_2.

Thorough micromorphological comparisons were also carried out using ESEM examinations. Thus for example Fig. 5 displays a comparison between details of the inscriptions of the coins C_{II} and C_2 where similar differences as above were observed. However, the univocal identification of minute details can be achieved only by means of a measurement of transverse profile. From this point of view, 3D videomicroscopy seems more suitable than electron microscopy although has a low magnification domain.

Thus for example, Fig. 6 shows a 2D profile of the coin C_1 along the white line of Fig. 4, where level changes with steps ranging between about 10–150 µm are observed. Similar 'stair' microstructures along with minute hardening bands and other marks were also found out on the coins $C_{I\text{–}III}$, and C_3, which supports the fact that these coins were struck.

4. Discussion and conclusions

The material data described above provide important information for assessing the authenticity of the coins investigated. The coins $C_{I\text{–}III}$ are composed of pure brass with a zinc content between 17–19 wt%, which is compatible with the know composition of Nero's sesterti. In particular, coinage brass (orichalcum) introduced during the Early Roman Empire had a zinc content between 20–25 wt%, which started to be reduced with Nero's reign [18].

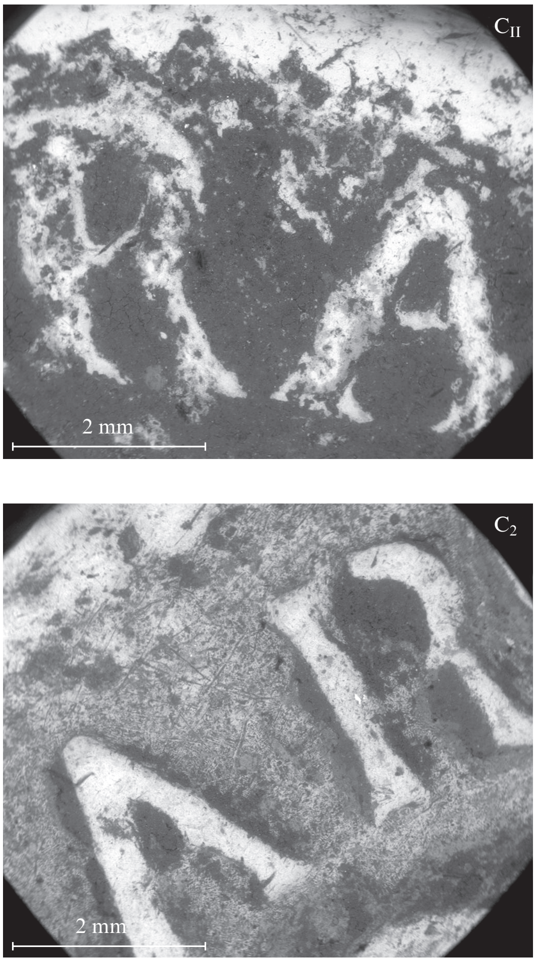

Figure 5. Comparison between the inscriptions on the coins C_{II} and C_2.

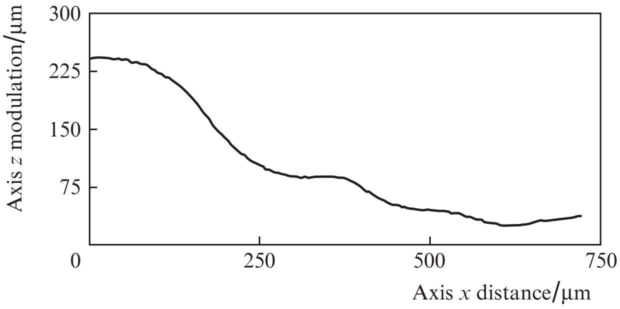

Figure 6. 2D profile extracted from the 3D relief of the letter 'A' on the coin C_1 along the white segment reported in Fig. 4. It shows a peculiar modulation produced by the dies during its striking.

3D videomicroscopy and ESEM examinations made it possible to point out a set of micromorphological features (Figs 4–6), which can be interpreted as marks produced by vibrations of the die during the striking process or by multiple hammering. These represent objective support to the numismatic authentication thesis even thought compatible composition and striking process alone cannot be considered a proof of authenticity. However, the analyses presented above also provide useful information about aging of the metal.

The coins $C_{I–III}$ had broad and structured compositional profiles. As we previously demonstrated, this is compatible with an archaeological provenience, whereas only moderate and/or localised surface modulations are usually observed for modern copper-alloy artefacts [5]. Besides the typical Zn profile showing a significant and relatively deep dezincification, such as that of C_{III} shown in Fig. 2, also more complex behaviours including depletion and enrichment phases were observed for $C_{I–III}$. As an example, Fig. 7 shows a Zn profile of C_I, which is very similar to that of C_1 reported in Fig. 2 but without a complete saturation to the stable bulk Zn content. Anyway, in all the cases (coins $C_{I–III}$) the amplitude and width of Zn wt% variations were significantly larger than those of the coins C_2 (Fig. 2c) and C_3. This represents a further and certainly sound result, which supports the authenticity of the coins $C_{I–III}$.

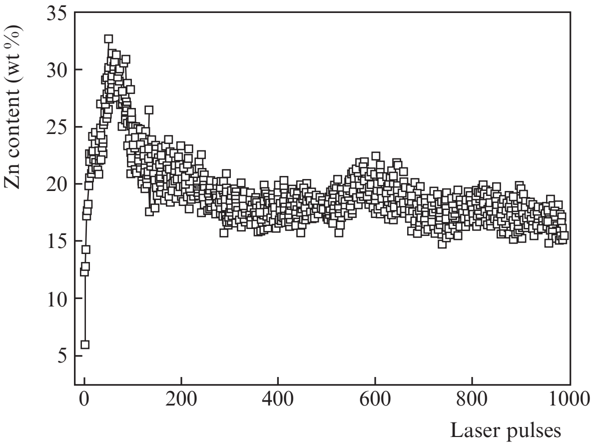

Figure 7. Zn depth profile for the coin C_I.

The coins $C_{1–3}$ were analysed using microscopy, LIPS and TOF-ND. The latter provided compositional data practically coincident with those of LIPS and clear evidence that the coins C_1 and C_3 were struck, since they exhibited a (100) fibre texture, which is systematically associated with unidirectional mechanical deformations of metals with an fcc lattice structure. Conversely, a weak cube texture was found in C_2, which proves the coin was cast in a mould suitably prepared and hence that it is a fake. Also its composition is incongruent with the typical one of Nero's sesterti although the significant compositional variability of ancient copper alloy coins, once again, does not allow using such a result tout court as an authentication criterion. On the other hand, compositional discrepancies certainly make stronger the objective proofs that a given artefact is a counterfeit. Furthermore, as displayed in Fig. 2 the Zn profile of C_2 is almost flat, i.e. the metal does not present any relevant corrosion phenomenology.

Despite the fact that C_3 was struck, its zinc content is rather lower than that of $C_{I–III}$ and the Zn profiles are only moderately modulated. This make it possible to conclude that the coin C_3 is a likely example of a massive forgery of the past centuries carried out using modern replicas of the ancient dies.

Finally, very interestingly the data of C_1 do not support the numismatic interpretation, which classified it as a fake. Besides the assessment of striking by means of TOF-ND, also composition and depth profiles support the authenticity of this coin. Its composition is very close to those of the coins $C_{I–III}$ and Zn depth profiles (Fig. 2) have strong initial modulations very similar to that of the coin C_I in Fig. 7, which stabilises to the bulk value only after about one thousand laser shots, corresponding to the depth of several hundreds of microns.

In conclusion, note that we preliminarily reported for the first time a novel combined approach to the authentication of ancient copper-alloy coins based on such noninvasive analytical techniques as TOF-ND, LIPS, ESEM, and 3D videomicroscopy. The combination of these techniques, provide a very effective way to assess manufacturing process, composition, and corrosion phenomenologies associated with aging.

Without any doubts TOF-ND represents the most elegant way to assess whether a coin was struck. On the other hand, this technique is hardly accessible and very expensive. For such reason, 3D microscopy was also included in the present work since it could represent a valid alternative to TOF-ND discriminating between cast and struck coins. 3D videomicroscopy allows recognising and measuring die marks, which are usually very hardly and univocally identifiable using common optical microscopy, as well as electron microscopy. Composition and corrosion were effectively assessed using LIPS, a microanalytical technique, which has a significant potential in archaeometallurgical studies.

Forthcoming works will be dedicated to the topic aimed at proving the effectiveness of very simplified authentication protocols entirely based on portable optoelectronic analytical tools.

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