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A multi-analytical approach for the identification of technological processes in ancient jewellery

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Abstract: The compositional and structural characterization of the constituent alloys of precious metal artefacts is the basis for understanding the technological processes used in the art of the ancient goldsmiths. This research presents a multi-analytical approach to the study of the technologies of ancient jewellery manufacturing through the use of non-traditional methods. The development of original methods, such as the application of hardware devices and software programs, allows us to overcome the application limits of traditional analysis, as in the study of Castellani's earrings, where statistical analyses were carried out using Pearson's Coefficient Correlation and Cluster Analysis to identify the correlation of elements in the soldering areas. For the Tarquinia fibula, a methodology based on Imaging Analysis has been used to measure the geometrical parameters involved in the construction of the jewel. For another study, a new experimental apparatus was set up in order to identify markers on the micro/nano scale. It consists of a scanning electron microscope (SEM-EDS) integrated with XRF, an equipment developed in order to obtain a greater depth of analysis and a better integration of the compositional data. The aim of the work has been to integrate data from different analytical methodologies in order to identify technology transfer and/or production features, as well as the circulation of the goldsmith's artefacts.

Résumé : *La caractérisation de la composition et de la structure des alliages en métal précieux est fondamentale pour la compréhension des procédés technologiques liés à l'orfèvrerie antique. Ce travail décrit un nouveau protocole d'analyse dédié à l'étude des technologies de fabrication de bijoux anciens, grâce à l'utilisation de méthodes non traditionnelles. Le développement de méthodes originales, utilisant entre autres des dispositifs expérimentaux et des logiciels, permet de dépasser les limites d'application de l'analyse traditionnelle. Par exemple, dans l'étude de boucles d'oreilles de la collection Castellani, l'analyse statistique réalisée au moyen du Coefficient de corrélation de Pearson et de l'analyse par nuage de points ont permis d'identifier la corrélation entre les éléments entrant dans la composition de la soudure. Dans le cas de la fibule de Tarquinia, une méthodologie basée sur l'analyse d'images a été utilisée pour mesurer les paramètres géométriques associés à la construction du bijou. Simultanément, un nouvel équipement a été créé pour individualiser des marqueurs à l'échelle micro/nanométrique. Il s'agit du couplage d'un microscope électronique à balayage équipé d'un système de dispersion en énergie X (MEB-EDS) avec la fluorescence à rayons X (FX) pour obtenir une profondeur d'analyse plus grande et une meilleure intégration et reproductibilité des données concernant la composition élémentaire. Le but de ce travail a été d'intégrer les données de différentes méthodes d'analyse afin d'identifier le transfert de technologie et/ou de travail lié à la production et circulation d'objets d'orfèvrerie.*

Keywords: Ancient technology, Etruscan jewellery, Image analysis, SEM-EDS-XRF system, Micro/nano diagnostic, Statistical analysis

Mots-clés : *Technologie antique, bijoux étrusques, analyse d'image, MEB-EDS-FX, Micro/nano diagnostique, analyse statistique.*

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1. Introduction

A deeper understanding of our cultural heritage is made possible through the contributions offered by scientific research. It is important to promote new research strategies capable of providing significant and potentially novel contributions towards the comprehension of the technologies used in ancient times, as well as of their transfer and diffusion in time across geographical areas.

Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) can be considered one of the most versatile instruments for analyses carried out in the field of cultural heritage, being able to provide data on almost all materials. The continuous development of instruments and their combination is necessary in order to detect data on the micro/nano scale, and for the interpretation of minute details from specific areas of an object. In the case of a jewel, it is necessary to go beyond the traditional information derived from SEM-EDS investigations by elaborating either the morphological information or the compositional data with methods derived from other disciplines, such as Image Analysis (IA) and statistical analysis (Cluster Analysis and Pearson's Correlation Coefficients). It is indispensable to improve traditional devices in order to create an innovative instrumentation able to acquire data generally inaccessible to forgers. In the present work, the coupling of the method of X-Ray fluorescence (XRF) with SEM-EDS, recently developed (Bovani *et al.*, 2007), is applied for the first time to the study of jewellery.

By focusing on the argument of falsification, the aim of the present work is to offer contributions towards two main directions:

– Innovation: improving traditional methodologies through the integration of experimental apparatuses, software and/or statistical methodologies for XRF-EDS compositional data treatment;

– Knowledge: the definition of diagnostic markers as characteristics of composition and/or morphology, and of chemical-physical processes allowing the identification of technologies of ancient jewellery manufacture.

The present work deals with the application of methodologies based on SEM-EDS through the study of some important Etruscan jewels: the 8th century BC fibula from Tarquinia (Fig. 1), a pair of *bauletto* earrings dating to the 6th century BC from Castellani's Collection, and a hoop earring from Adria, dated to the 4th century BC (Fig. 2).

2. Methods

Investigation on the micro/nano scale is essential for the identification of diagnostic markers related to particular processes applied to materials, ranging from prehistoric lithic tools to the trimmings of large bronze statuaries. In the case of metals, this entails identifying the traces left during the working process, regardless of the metal employed and its specific structural modifications, due to thermal processes or mechanical stress and strain. Particular attention must be dedicated to distinguishing degradation phenomena, such as the formation of corrosion products or use traces, which can be confused with those left by the craftsmen of the past. A specific diagnostic approach is necessary for each artefact.

3. Results

Concerning the study of the fibula (Fig. 1) found in an archaeological excavation in Tarquinia (Rome) and dated to the 8th century BC (presenting some details not pertinent to traditional Etruscan jewellery), the scope of the scientific investigation was the characterization of decorative elements, granulation and filigree, through their geometrical and compositional parameters and their comparison with homologous decorations from the Mediterranean area. In a previous work (Ferro *et al.*, 2005), a comparison of objective elements present among different technologies employed in the creation of some jewels originating from different geographical areas (Iran, Cerveteri, Adria, Syria) in the temporal range 21st century BC-3rd century AD, was carried out.

Figure 1: Etruscan fibula, 8th century BC, Tarquinia (Viterbo, Italy).
Figure 1 : Fibule étrusque, VIIIe siècle avant J.-C., Tarquinia (Viterbo, Italie).

Figure 2: Attachment of the Etruscan hoop earring, 4th century BC, Adria (Rovigo, Italy).
Figure 2 : Boucle d'oreille étrusque, IVe siècle avant J.-C., Adria (Rovigo, Italie).

SEM-EDS analyses provided information on the morphology of the grains forming the granulation decoration and on the elemental composition of the areas characterizing a particular technology, such as mechanical joining, soldering and sheet working. In addition, the geometrical characterization of the small and numerous grains was carried out using Image Analysis (IA) of the SEM micro-photographs.

IA analysis is not so straightforward when applied to SEM images. For processing the software elaboration (Leyca QWin), it is necessary to establish an appropriate methodological approach that includes specific steps (Fig. 3). The acquisition of SEM images must be made with an adequate mode of contrast and magnification. The necessary linear measurement calibration data has to be determined on images taken with stereo microscopy, optic microscopy and SEM in order to evaluate the degree of error involved. In order to optimize the results, the images were submitted to an elaboration that comprises enhancement, threshold and selection of grain profiles characteristics so as to allow diameter measurements with a minimum of uncertainty.

The characterization of the grains' shape, roundness, or rather the eccentricity in the bi-dimensional image, was determined by introducing the values of two orthogonal diameters in the ellipse equation. The second evaluation regards grain packing in the granulation decoration. The covering of a surface is of superior quality if most of the grains are in touch, without noticeable gaps between them. By considering grains as spherical geometrical elements, the concept of sphere packing can be applied. It is obvious that if the diameters of grains have different dimensions, the decorative motif contains pattern displacements. The surface is not covered homogenously, but shows discontinuity, thus diminishing the object's overall aesthetic effect. For the granulation of each jewel, the average diameter and its standard deviation (σ) have been calculated by the approximation of measurement data to Gaussian distribution using the "Origin" software. The standard deviation measures the variation in terms of diameter size from its mean value, and indirectly reflects on the goldsmith's ability to produce and select grains of the same dimension and roundness.

Another evaluated granulation feature is its 'tridimensional' effect, related to the position of the gold grains in relief with respect to the jewel's surface. This effect is linked to thermal processes of grain soldering. A previous study (Ferro *et al.*, 2003) demonstrated that, especially in autogenous soldering, the granules tend to collapse into the surface support if the heating is prolonged and the surface of the grains and gold substrate start to melt (excessive surface flowing). In copper salt joining, the Cu that originates from the reduction of its salts diffuses in gold, and little material is left on the join, a fine meniscus formed between the base and the grain (Ferro *et al.*, 2008), creating the effect of spheres per-

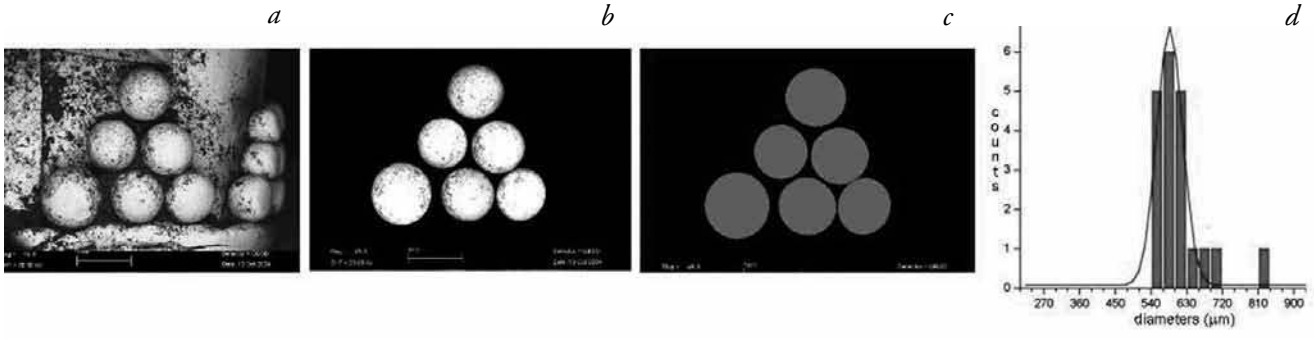


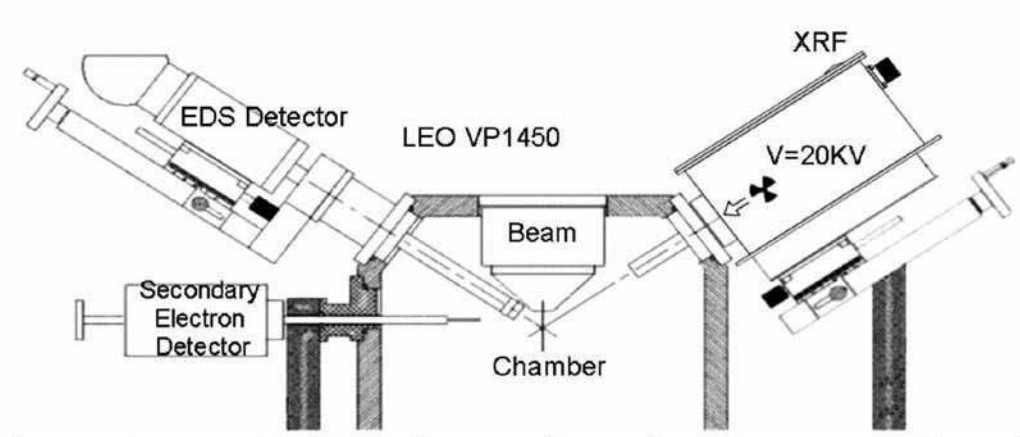
Figure 3: Several steps of Image Analysis: a) SEM image acquisition, b) binarization, c) selection of features, d) statistical analysis.
Figure 3 : Différentes étapes d'analyse d'images : a) acquisition d'une image MEB, b) binarisation, c) sélection des caractéristiques, d) analyse statistique.

ched on a base. Conversely, brazing by adding an alloy with a lower melting point partially floods the grains, with the consequent loss of tridimensionality and design.

In this work, five independent parameters have been selected to distinguish different granulation scenarios: 1) join typology (welding), 2) diameter average, 3) diameter standard deviation (σ), 4) grain eccentricity (circumference has eccentricity = 0), and 5) tridimensional effect. All these parameters provide a collection of data that characterizes the physical features of grains and their clustering, and can thus be utilised as diagnostic markers for distinguishing jewels from different geographical regions and historical periods. The results of the investigation have shown that in the Iranian and Syrian jewellery, the grain diameters are of the order of 700 microns, with a standard deviation of about 90 microns, an eccentricity of 0.04, and have identified the use of brazing as a soldering methodology, with a consequent loss of tridimensionality. In the Etruscan area, the average diameter is reduced to about 200 microns, with a standard deviation of 65 microns and eccentricity of 0.02. Etruscan granulation is characterized by the use of copper salts in most cases. After 300 BC, Etruscan jewellery shows a general loss of precision in terms of roundness, even though grain dimensions remain very small and the use of the copper salt soldering continues. The results obtained for jewels in the previous study are reported in Table 1. Concerning the Tarquinia fibula (Fig. 1), made in electrum, the same procedure has been applied, with the resulting parameters attributable to a working process of oriental derivation: the average diameter of 650 microns, with a standard deviation of 70 microns, the high incidence of non-spherical grains, the lack of tridimensionality, and the use of brazing as a soldering method. This data, coupled with other stylistic observations, such as the shape of the Phoenician *palmette*, the use of filigree wires cut at a right angle, and the imperfect form of the pin clasp, supports the archaeologist's hypothesis of a possible oriental origin of the working process employed for this object, found in an Etruscan context.

In other studies, superficial characterization is not sufficiently exhaustive for the complexity of the investigation, and it is necessary to resort to radiation analyses in order to obtain information from the entire volume of the sample. In this field, an integrated instrumentation that integrates electron microanalysis (EDS) and X-ray fluorescence (XRF) within the SEM environment has been developed (Bovani *et al.*, 2007). The SEM-EDS-XRF (Fig. 4) setup was created by inserting in the SEM LEO450VP chamber a tungsten anode X-ray tube with a geometry of 45° with respect to the sample and 90° with respect to the solid state (SiLi) detector, the latter having an active surface suitable for detecting X-ray signals originating from both systems. The advantages derived from the use of an integrated instrumentation are notable, such as the increase of sensitivity in the detection of trace elements. XRF reveals element quantities of the order of ppm, and it is possible to detect signals both from the first superficial layers (EDS) and from the inner volume (XRF). When used in an SEM environment, XRF warrants better efficiency with respect to its separate use for several reasons, from a suitable fixed geometry to the operability in high vacuum by avoiding the absorption of low energy X-rays. INCA300, the EDS signals processing software, supplies an optimum support to XRF through an X-ray energy spectra calibration obtained by standards.

The characteristics of both devices allowed discriminating the presence of different phases in the precious hoop earring from Adria, dated to the 4th century BC (Fig. 2), where several metal laminas overlap and different materials have been employed for its construction. The earring, approximately 5 cm in diameter, is composed of a cylindrical tube formed by the torsion of several wires, each of which is produced with rolled lamina. The terminals of the 'tube' are decorated by two small gold lamina cylinders with granulation and are joined to two semi-spheres in gold lamina, found partially crushed. Stylistic and geometrical considerations on the technique used to decorate the object with granulation have been derived on the basis of the previously described methodology, revealing its appurtenance to the period of Etruscan decadence. The grains, fixed by autogenous welding, have small diameters, but their dispersion is very bad, with the sole function of covering the soldering area, without any pattern. The unusual dimensions of the earring are in contrast with its light weight. The filling material in the inner part of the cylinder was likely used to preserve the form and avoid damage to the fine wire wrapping. The traditional X-ray radiography with a radiation potential of 30 keV allows us only to individuate the presence or absence of any filling materials, but not its chemical nature. The presence of a continuous compact matrix in the cylinder and inside the two semi-spheres appears evident in photographs, despite the impossibility to penetrate through the wrapped gold wires without compromising the artefact. The investigation with the integrated EDS-XRF system was tested in order to verify the hypothesis of the presence of some filling material. The EDS data revealed only the composition of the gold metal surface constituting the object, while the XRF spectra detected the presence of elements characteristic of 'earth'. It is important to note that the XRF method operating in the SEM chamber kept under high vacuum can also detect low energy X-ray emissions. On the basis of the collected data, it is plausible that the goldsmith used a clay



	Signal	Element Range	LOD	Depth	Lateral resoution	Image
SEM-EDS	SE and BSE	B – U	0.1 – 1 at%	1 – 5 µm	4.5 nm (SEM); 1 µm (EDS)	Yes
XRF	Raggi X	Na – U	100 ppm	10 µm	100 µm	No

Figure 4: Scheme of experimental instrument SEM-EDS-XRF.
Figure 4: Schéma du dispositif expérimental MEB-EDS-FX.

Object	Dating	Origin	Welding	Three-dimensionality	Average of diameter ± σ(*) µm	σ of diameter µm	Eccentricity
Pendant PREIS. 9	ca. 2000 BC	West Iran	autogenous	moderate loss of definition	587 ± 14	65	00:04
Pendant PREIS. 36	2000-1000 BC	Iranian plateau	autogenous	moderate loss of definition	782 ± 18	97	00:03
Tarquinia's Fibula	8th century BC	Tarquinia	brazing	moderate loss of definition	653 ± 15	70	—
Earring PREIS.47	3rd century AD	Iranian plateau	brazing	moderate loss of definition	519 ± 8	66	00:04
Fibula Inv. N. 5442	7th century BC	Narce	copper salt	good	242 ± 8	50	00:02
Pendent IGAD 9295	3rd century BC	Adria	copper salt	good	160 ± 24	147	00:07
Bulla IGAD 9306	2nd century BC	Adria	autogenous	good	727 ± 37	149	00:03

(*) *The errors have been calculated as standard deviation and through statistic error propagation.*

Table 1: Table of comparison parameters.
Tableau 1: Tableau de paramètres de comparaison.

rod on which he wrapped the series of gold wires. The clay would have two functions: first, to create a support enabling the object to maintain its shape, and, second, to protect the very thin gold lamina forming the wires from the heating processes necessary to solder the terminal elements.

The study of the Etruscan *bauletto* earrings (6th century BC) from Castellani's Collection (Museo Nazionale Etrusco di Villa Giulia, Rome) is more complicated. The earrings under consideration are an example of pastiches: an original Etruscan jewel with repairs carried out by the Castellani, a Roman family of goldsmiths, merchants and collectors operating during the 19th century. The respective century was characterised by the proliferation of so called 'integrative' restorations, i.e. the restitution of the full shape of a historical object so as to introduce complete archaeological artworks on the antiquarian market, because customers valued the integrity of an *object d'art* over its authenticity. The Castellani family studied, reproduced and restored ancient jewels, and contributed to the spreading of the Italian archaeological jewellery style (Moretti Sgubini, 2000). With the aim of individuating the restored elements integrated into genuine Etruscan jewels, an initial study was undertaken on a contemporary pair of earrings produced by Castellani in the 19th century, in order to identify

the characteristics and the tool traces of their *officina*, and subsequently to recognize 'their hand' on restored objects. A local heating process that partly homogenized the alloy on a micrometric scale and caused a modest compositional variation renders a precise delimitation of the Castellani interventions problematic.

With the purpose of interpreting, distinguishing and identifying the correlation among the chemical elements composing the gold base, the decorative elements and their soldering area, the statistical analysis has been carried out using Pearson's Correlation Coefficient and Cluster Analysis (Virgili *et al.*, 2008). This statistical tool has been processed with SPSS 8.0 software on the data collected by several EDS acquisitions. Pearson's Correlation Coefficient is a measure of the linear dependence between two elements of precious alloy identified as variables, and allows distinguishing whether an element belongs to a specific procedure rather than another. The K-Means Cluster Analysis (Romesburg, 2004) aims to classify groups of homogeneous elemental composition in order to identify the alloys composing ancient and modern soldering and the different areas of ancient and modern brazing. For the earrings created by Castellani in the 19th century, the elaboration of the statistical data has been performed on 74 spectra acquired on different areas, previously selected on the basis of their technical content. Pearson's correlation matrix of elements of the precious alloy shows a high negative value of linear dependence between Au and Ag. This evidence suggests that the soldering alloy had a higher silver content. Copper does not seem to participate in the chemical-thermal reactions, while the presence of cadmium points to its probable use in the form of cadmium mineral (CdS). The yellow colour of both the metal and the mineral also suggests its use to camouflage the gold soldering. The cluster analysis allowed evaluating the elemental composition of the lamina and the soldering area. Cadmium is present only in the soldering areas, with a variable percentage of circa 1%.

In the analysis of the other pair of earrings from Castellani's collection "ori antichi", each piece was studied individually, so as to determine the composite nature of each artefact. One of the two earrings (referred to as A) presents clear signs of restoration. A different decorated lamina has been added on the recto and fixed by filling it with organic materials, such as binder and fibre. In this item, Cd is absent, and the linear dependence Au-Cu demonstrates the use of copper soldering, a technology typical of Etruscan manufacture, while the one between Au-Ag emphasizes the presence of silver joining, characteristic of the Castellani production. This suggests that the Castellani soldering interventions were superimposed on those of the Etruscan artisan, probably because the joining parts are the most vulnerable in time. In the other ancient earring (B), the most significant evidence is Au decrement with respect to the Cu and Cd concentrations, as revealed by the variables correlation analysis. There is no direct proportionality relation detected between Ag and Cu. This implies that in the analyzed areas the two elements are not correlated. The evaluation of the results suggests the exclusion of the possibility of any Ag-Cu alloy utilization, and the consequential presence of copper salt soldering areas altered by 19th century interventions employing cadmium. The study on the Castellani collection earrings has induced us to hypothesize that not only had a novel procedure been adopted in their *officina*, but that experimentation had been undertaken and applied to the production of modern jewels, as well as to the restoration of ancient Etruscan artefacts. The results obtained by the application of statistical analyses to the EDS compositional values are summarized by visualizing (Fig. 5) the areas where the Castellani interventions (highlighted in red) were performed versus the original Etruscan structure (highlighted in green).

Figure 5: (See colour plate) *Bauletto* earrings, 6th century BC, Cerveteri (Rome, Italy). The modern items are highlighted in red, and the ancient ones in green.
Figure 5 : (Voir planche couleur) Boucles d'oreille "a bauletto", VIe siècle avant J.-C., Cerveteri (Rome, Italie). Les éléments modernes sont mis en évidence en rouge et les anciens en vert.

4. Discussion and Conclusions

The integration of scanning electron microscopy (SEM) with other techniques, such as the simultaneous use of X-ray fluorescence operating in an SEM chamber, computer elaboration of image analysis, or statistical methods for the EDS microanalysis data treatment, transforms the microscope into a potent analytical tool capable of providing data not detectable with traditional diagnostic methodologies, thus promoting a new vision on the identification of fakes.

In this work, some cases have been presented in which the electronic spectroscopy data has been interpreted in a different way, with the support of specific analytic approaches. In the study of the composition of different granulation decorations, the possibility to establish selection criteria for the interpretation of the ancient techniques employed led to the formulation of a methodology based on the definition of five characteristic elements: 1) grain diameter, 2) grain roundness, 3) frequency of the average value of the diameter, 4) soldering chemical composition, and 5) tridimensionality. This methodology, applied to the study of gold items originating from different geographical areas, allowed us to establish important considerations on the fibula from Tarquinia. This information, integrated and completed by philological and historical-artistic studies, contributes to the discussion of technological transfers of craftsmen's abilities and manpower, the diffusion of procedural recipes, and the trade of jewellery in the Mediterranean Basin.

The use of an integrated instrument created by inserting an X-ray tube in the SEM chamber offered the possibility to analyze both the surface and the inner part of the earring from Adria, and furnished important data for the attribution of the nature of the constituent materials, which in turn may be considered a valid support for an eventual restoration.

A statistical approach has been employed for the elaboration of the numerous data related to the composition of the restored areas in two Etruscan earrings from Castellani's Collection, resulting in a new diagnostic interpretation.

A concise, tailored description of a precious object, integrated with historical, iconographic and artistic evaluations, is the most effective 'weapon' in the 'war' to identify counterfeits.

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