NON-INVASIVE, SCIENTIFIC ANALYSIS OF 19TH-CENTURY GOLD JEWELLERY AND MAIOLICA. A CONTRIBUTION TO TECHNICAL ART HISTORY AND AUTHENTICITY STUDIES

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INTRODUCTION

The present research on Geomaterials and their application in Cultural Heritage was developed at the University of Florence in collaboration with the Centro Nacional de Aceleradores of Seville, the Victoria and Albert Museum (V&A) in London and the Museo Nazionale Etrusco di Villa Giulia in Rome. The subject of the PhD project was the compositional characterisation, by means of non-invasive analyses, of gold jewels and maiolica wares (*i.e.*, tin-glazed earthenware) in historicist style produced in Italy in the 19th century with the aim of providing a contribution to technical art history and authenticity studies.

Artefacts made in the 19th century have been largely overlooked in archaeometric and heritage science studies and there is a significant lack of published data on the materials used for their production. Nevertheless, the 19th century is a fundamental period when dealing with art and archaeology. In fact, the century was characterised by significant archaeological discoveries, which deeply influenced the culture of the time from an artistic, social and even political point of view.

Archaeological artefacts were studied (both from a stylistic and from a technological point of view), traded, copied, and forged, with the antiques market reaching unprecedented levels. Another result of this fascination for antiquities was the development of the Revival (or Historicist) style, based, indeed, on the copy and reinterpretation of ancient art by modern artists. It is on this kind of production that the present research is focused, and, specifically, on maiolica and gold jewellery, which were two classes of materials extremely popular at the time (Fig. 1).

Another important feature which characterised the 19th century was the development of the chemical industry, which made new materials available on the market. The research aimed at understanding which of these newly-introduced materials started to be used in the production of maiolica and gold jewellery along the century.

Aims of the study

The aim of this study was primarily to increase our knowledge of the history of technologies and artistic techniques and their development in this period of transition from a traditional production to a modern one. Moreover, the analysis aimed at the characterisation of the working practices of some of the most important revival artists of the 19th century, especially focussing on the choices made by artists in the process of imitation of ancient art. This information constitutes an important reference for authenticity studies, since numerous forgeries were produced in the 19th century and it is not uncommon to find them in public and private collections.

Case studies and methodology

Two case studies were selected:

1) the jewels, today at the Museo Nazionale Etrusco di Villa Giulia in Rome, made by the Castellani, the most popular goldsmiths in 19th-century Europe, who invented the style known as ‘Italian archaeological jewellery’ (Bordenache Battaglia *et al*., 1978; Moretti Sgubini, 2000; Weber Soros & Walker, 2004);

2) the maiolica wares, part of the collection of the Victoria and Albert Museum (V&A) in London, made in Neo-Renaissance style by the Ginori and the Cantagalli manufactories, the main promoters of the revival of Italian maiolica (Frescobaldi Malenchini & Rucellai, 2011), and by the ceramist Torquato Castellani, member of the above-mentioned family of goldsmiths (Cristini, 2007).

Fig. 1 - Examples of an original jewel and a maiolica ware (left) and their 19th century imitations (right) analysed in this study. Top: A medieval buckle is shown on the left, while its reinterpretation made by the Castellani goldsmiths is shown on the right (Castellani Collection, Museo Nazionale Etrusco di Villa Giulia, Roma). Bottom: A roundel made in Gubbio in 1525 is shown on the left, while the copy made by Torquato Castellani in 1870 is shown on the right (© Victoria and Albert Museum).

From a methodological point of view, the first challenge to be addressed in the planning of the analysis was that the investigation of intact objects in museum collections required the use of non-invasive, *in-situ* analyses. X-Rays Fluorescence spectroscopy was selected as the best method to analyse both gold jewellery and maiolica.

This technique is based on the phenomenon of X-Rays Fluorescence, that is on the emission of characteristics X-rays by atoms excited by a primary X-rays beam. It allows the identification of most elements constituting inorganic materials in a completely non-invasive way. Portable XRF instrumentation is available and the relatively short acquisition times allow to investigate a high number of areas.

Two different XRF set-ups were used (and partially upgraded) in this study to analyse the gold alloys and joining techniques used in Castellani jewels and the glazes of historicist Italian maiolica, respectively, and will be described more in detail below. It must be underlined that, using non-invasive analysis, it was possible to analyse only the surface layers of the artefacts.

GOLD JEWELLERY

Materials and methods

The Museo Nazionale Etrusco di Villa Giulia boasts the most complete and broadest collection of Castellani jewels: 43 jewels made between the 1840s and the 1890s were selected for this study, in order to cover the widest range of styles and techniques as possible.

The analysis of gold jewellery is extremely challenging (Guerra, 2008). The Castellani jewels were analysed inside the museum using the portable micro-XRF spectrometer built in house by the researchers of the Centro Nacional de Aceleradores (CNA) of Seville specifically for the analysis of ancient jewels (Scrivano *et al.*, 2017). Thanks to the use of polycapillary lenses, the primary X-ray beam is focused on the sample on a spot as small as 30 µm and allows the separate characterization of the gold foils, wires, granules and soldering areas. Moreover, the CNA spectrometer was modified for this study with the addition of a second detector with a zinc filter (Fig. 2).

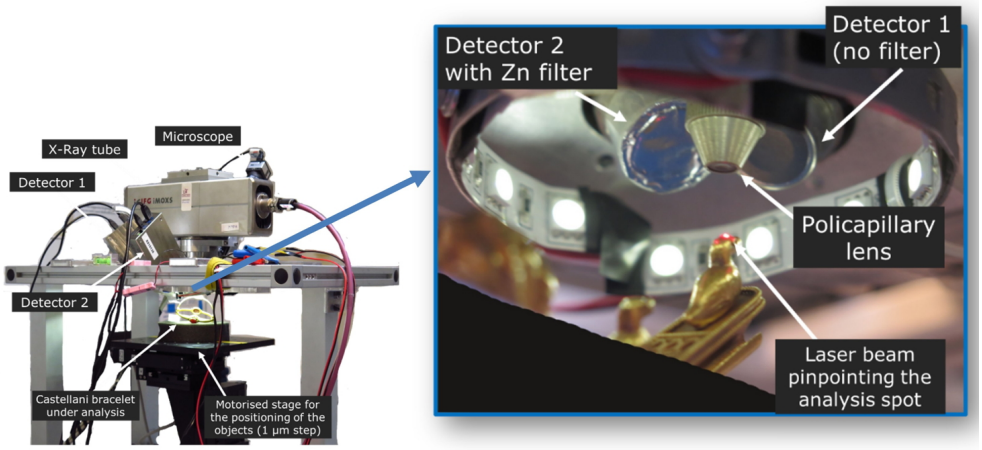

Fig. 2 - The CNA XRF spectrometer. A close-up of the analysis area is shown on the right.

As described by Ortega-Feliu *et al.* (2020), the use of a zinc filter in front to the X-ray detector attenuates the signal from gold, thus hindering the formation of the gold sum peaks, which interfere with the characteristic X-rays lines of some elements. In this case, the use of the zinc filter was fundamental to check the presence of cadmium (Cd Kα line at 23.11 keV), an element first identified in 1817 and added to brazing alloys only from the second half of the 19th century (Meeks & Craddock, 1991).

The analysis was performed at 50 kV and 600 µA, for 300 s acquisition time. A set of *ca.* 1390 spectra was acquired from the Castellani jewels and was analysed and quantified using the open-source softwares WinQXAS and PYMCA.

Results and discussion

The analysis showed that high-carat gold (*ca*. 80-99 wt.% Au), with silver as the main alloying metal, was used by the Castellani (Fig. 3). This result was in contradiction with a paper published by Fortunato Pio Castellani in 1826, in which he stated that the most common alloy used by him and his contemporaries was 18-carat gold (75% Au content) with copper as main alloying metal (Castellani, 1826). However, in the same paper he also wrote that, according to him, ancient goldsmiths were using either pure gold or alloys of gold and silver. It is therefore possible that the intention of imitating ancient jewels influenced Castellani's choice of materials and lead them to use alloys of gold and silver even if they were not the most common at the time.

As for the soldering techniques, the different elements of the jewels, including granules, were soldered with brazing alloys rich in silver. Cadmium was never detected in the joining areas analysed, indicating not only that cadmium-containing solders were not used by Castellani, but also that forgeries where cadmium was detected in previous studies (Meeks & Craddock, 1991; Formigli & Heilmeyer, 1993) are not likely to have been produced by Castellani, or at least not by the same Castellani workshops where Villa Giulia jewels were made. In only two cases, the analyses showed that the granulation was not soldered but glued to the base foils with an organic resin containing metallic driers.

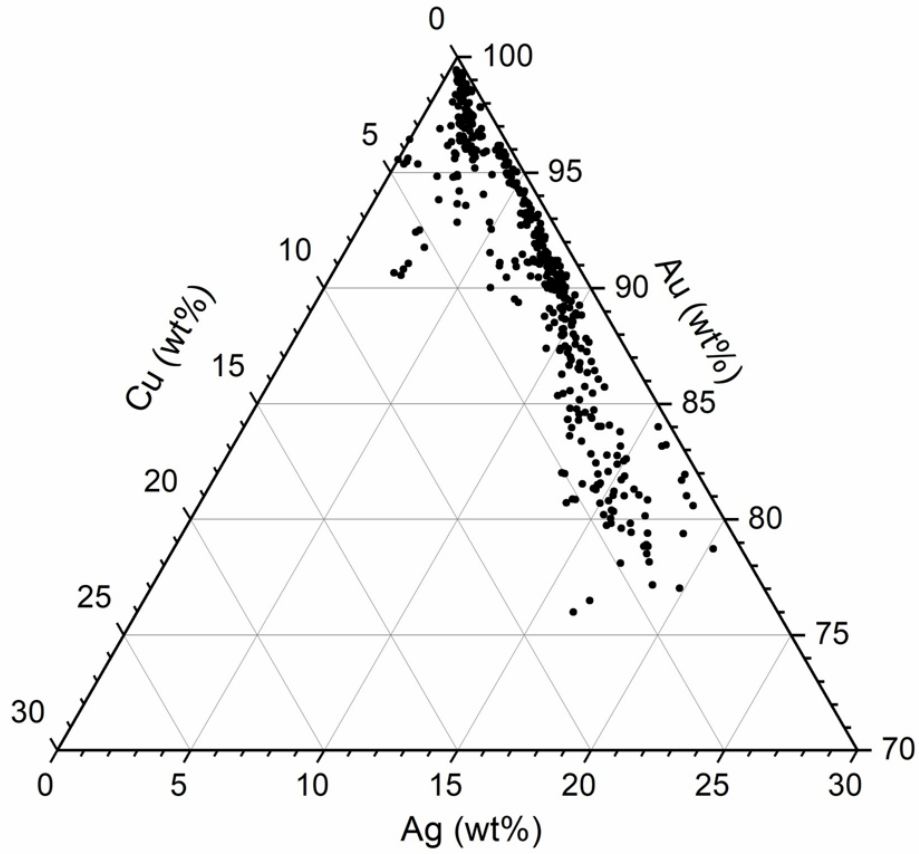

Fig. 3 - Ternary diagram showing the composition in terms of gold, silver and copper (wt.%) of the analysed foils of the Castellani jewels.

Finally, a topic of great interest when dealing with Castellani jewellery is their use of 'colouring' treatments, *i.e.*, the application of etching solutions on the gold alloy to remove the copper and silver content and obtain a final enrichment in gold in the surface layer. A method based on the study of the relative intensity of the different X-rays lines of gold in the XRF spectra was tested in this study, in the attempt of determining the presence of compositional gradients from the surface to the subsurface of the jewels by non-invasive analysis. The relative intensities between the lines of the same element are always constant in a homogeneous sample and using the same working conditions.

On the contrary, the ratios between these lines change in case of compositional gradients going from the surface to the subsurface, depending on the energy of the line and on the depth from which this line is produced. The ratios L3/M and L2/L3, which are expected to be lower if the surface is richer in gold than the subsurface, were taken into consideration.

The values obtained from the Castellani's jewels tend indeed to be lower of those of homogeneous standards taken as a reference. This result suggests the presence of a surface enrichment in gold in most Castellani's jewels, which is compatible with the use of 'colouring' treatments.

MAIOLICA

Materials and methods

The V&A hosts an important collection of Italian maiolica. Twenty-one Neo-Renaissance wares made in the 19th century were analysed. They are mostly signed and dated and were made between 1855 and 1900. In addition to them, three original Renaissance wares were analysed for comparison.

The analyses were performed using the commercial XRF spectrometer (Roentec-Bruker ARTAX) available in the V&A Science Section. The spectra were acquired at 50 kV and 600 μA, for 200 s acquisition time. The elemental composition of the white ground glazes, the coloured glazes and the lustre decorations was determined. Quantitative analysis was not performed in this case: only semi-quantitative evaluations were made by comparing the intensities of peaks of the same elements from different samples or from different areas of the same sample.

Results and discussion

The compositions obtained from the wares by Ginori, Castellani and Cantagalli were overall similar to that of Renaissance maiolica (Tite, 2009), being characterised by the presence of lead oxide and alkali as fluxes, lime as stabilizer, tin oxide as opacifier and traditional colourants and pigments (*i.e.*, copper green, manganese brown, cobalt blue, antimony yellow, tin oxide, copper and silver lustres). This indicated that, when reproducing Renaissance maiolica, revival ceramists were imitating not only its style, but also its materials and techniques.

However, a few modern materials were also detected. In particular, zinc was detected in most of the 19th-century wares analysed, and was particularly abundant in the later ones made around 1900. Zinc oxide improves the optical and rheological properties of tin glazes and became commonly available only in the 19th century. The broad presence of zinc is the main feature that differentiates the 19th-century glazes analysed from Renaissance maiolica glazes, which otherwise have a remarkably similar composition. The comparison with Renaissance maiolica was based both on the data available in the literature and on the XRF analysis of three V&A wares: two original pieces which inspired a Cantagalli and a Castellani copy, respectively, and a 16th-century plate with 19th-century replacements.

Beside zinc, only a few modern elements, available thanks to the recently-established chemical industry, were identified. Chromium-containing colourants were detected in only four objects by Castellani and Cantagalli. Interestingly, chromium was never detected in Ginori objects, while the study of the historical archives of the Ginori Manufactory revealed that chrome green was bought from Paris as early as in 1840; this indicates that chrome colourants were available but intentionally not used in artistic maiolica. Finally, lustre decorations containing gold, bismuth and uranium, instead of the traditional metallic copper and silver, were identified in the dish with Graces made by Torquato Castellani in 1870 (Fig. 1, right). By that year it was known that Renaissance ceramists used copper and silver to obtain their astonishing lustres decorations: this indicates that Castellani intentionally chose to experiment with new materials instead of imitating the traditional technique.

Finally, the analysis of one of the Renaissance objects analysed offered an interesting opportunity to use the data acquired in this study as a reference for attribution studies: this plate, depicting a birth scene was made in Urbino around 1545, but it was extensively restored in the 19th-century, when three fragments were attached to the main body (Fig. 4). According to the V&A curator, the replaced parts had been possibly made by Ginori in 1860. The analysis of both the original part and the 19th century additions showed that one fragment (n. 2 in Fig. 4) has exactly the same composition as the main body, suggesting that it is an original part simply reattached to the plate. On the contrary, the other two fragments showed a different composition both from the main body and from all the Ginori wares analysed in this study. This result suggests that it is unlikely that the restoration was made by the Ginori manufactory.

CONCLUSIONS

In conclusion, the analytical results obtained in this study represent the most extensive set of compositional data on both 19th-century gold jewels and maiolica and constitutes a solid basis for a prosecution of the scientific research on this unexplored subject, paving the way to future studies on 19th-century artefacts of different styles, makers and provenances, and testing the use of other non-invasive analytical techniques.

This research provided precious information on the production practices of some of the most popular and influential goldsmiths and ceramists of 19th-century Europe, revealing a balance between ancient and modern,

i.e., between the attempt of imitating ancient techniques and an attention to the modern innovations of the chemical industry.

Fig. 4 - Maiolica dish with birth scene probably made in Urbino around 1545 and restored in the 19th century. The red lines show the profiles of the three fragments. (© Victoria and Albert Museum, object n. C.2223-1910).

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