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Non-invasive archaeometallurgical approach to the investigations of bronze figurines using neutron, laser, and X-ray techniques

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ABSTRACT

In the present work, structural imaging and non-invasive compositional analysis have been successfully combined in order to investigate three bronze figurines from the antiquarian collection of the Egyptian Museum of Florence. High-resolution neutron tomography was exploited for a thorough reading of the technological features of the mentioned copper alloy statuettes. At the same time portable XRF–XRD, Raman spectroscopy, laser-induced plasma spectroscopy, as well as time-of-flight neutron diffraction provided a powerful complementary analytical set for achieving reliable surface, depth profile, and bulk analyses. The proposed multi-analytical and non-invasive approach, involving neutron, X-ray, and laser techniques, allowed exhaustive identification of the raw materials and interpretation of the crafting processes used by ancient bronze smiths.

1. Introduction

Ancient Egyptian metallurgy represents a milestone in the development of metal-working and casting practice, and its fundamental importance has been recognized since the beginning of the XX century [1,2]. In the past, bronze figurine production methods and materials have been understood in large degree from extensive studies of ancient samples by means of traditional sampling techniques followed by elemental analysis ([3,4] and references therein) or metallography [5]. Nowadays, a considerable technological advance and the development of best practices in the preservation of cultural heritages allow the characterization of object of interest in a non-destructive way. Imaging techniques, including standard X-ray or the somehow complementary neutron radiography or tomography (NT) [6], have been applied in the study of metal artifacts of historical interest [7–10]. They can provide information about the material distribution, composition, manufacturing, and alteration process. However, for a clearer picture about the composition of the materials involved, other analytical techniques are usually needed [11]. Elemental techniques such as X-ray fluorescence (XRF) and ion beam analyses or molecular techniques such as X-ray diffraction (XRD) have been used in the characterization of Egyptian bronzes surfaces, mostly for the study of corrosion products or surface treatment (patination, gilding, etc.) [12–17]. On the other side, time-of-flight neutron diffraction (TOF-ND) can provide compositional and micro structural data averaged over large measurement volumes (in the order of cubic centimeters) [18–21]. Laser-induced plasma (or breakdown) spectroscopy (LIPS or LIBS) [22] fills the gap between the above-mentioned surface techniques and the TOF-ND bulk analysis since it provides spatially resolved measurements (in the order of hundred microns) in the form of quantitative elemental depth profiles. Each laser pulse ablates a certain amount of the material and thus penetrates step by step into the sample. The spectra of the successive laser pulses are processed to obtain the element distribution in depth. LIPS is therefore considered a micro destructive technique (typical ablation diameter of 100–200 μm), but its invasiveness is likely negligible in most applications, even in the cultural heritage domain [23].

Here neutron imaging (NT) and diffraction (TOF-ND) as well as complementary compositional analysis (LIPS, XRF, Raman spectroscopy, and XRD) have been successfully combined in order to investigate three bronze figurines from the antiquarian collection of the Egyptian Museum of Florence. This allowed exhaustive identification of the raw materials and interpretation of the crafting processes used by ancient bronze smiths. The selected artifacts presented some peculiarities, which made them representative of a broad class of archaeometric investigations. Preliminary X-radiographic analysis allowed arguing that one of them, representing the goddess Neith, contained intact casting cores, while another one, representing a nursing Isis, was emptied of the casting cores from visible openings, and the third, representing the Horus Falcon, contained some residual materials. However, X-radiography did not allow a sufficient image contrast needed in order to decipher the manufacturing procedures and state of conservation. Casting cores in

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Egyptian bronzes typically were left intact (see for example [24]), unless the pieces were intended to function as sarcophagi, which is the case for many of the hollow-cast animal figures. As an example, which is of interest for in the present investigation, several falcon bronze sculptures in the Walters Art Gallery collection in Baltimore, Maryland, were analyzed using thermal neutron radiography and most of them seemed to contain bird remnants or mummy bundles [25]. This organic material showed up in the neutron radiograph because some of the light chemical elements present in them, particularly calcium, nitrogen, and hydrogen, posses a high neutron attenuation coefficient. However, it must be stressed that a clear identification of bird bones was only possible in one sample thanks to a direct visual inspection via an endoscope inserted into a small hole in the head of the falcon. Our falcon sample does not present any aperture and we exploited for the first time high-resolution neutron tomography and TOF-ND in order to visualize such remnants deposited in an inaccessible bronze cavity, and give some insights on their composition.

2. Materials and methods

The samples used in this work to demonstrate the potentialities of the integration of the above-mentioned techniques in archaeometallurgical studies are three bronze figurines from the Egyptian collection of the Archaeological Museum of Florence (Fig. 1). The largest one (inv. N.8401) was a bronze falcon ($15 \times 6.5 \times 15$ cm) on a wooden base ($7.5 \times 10 \times 24$ cm), which was a standard representation of the god Horus in ancient Egypt. It has unknown origin and was inherited by the museum from Bartolucci legacy in 1892. The surface appeared of dark brown/reddish tone with evident signs of corrosion especially on the left side where earthy material and green corrosion compounds are mixed. Nevertheless fine details of the crafting process such as the engraved feathers were still visible and overall it was in reasonably good state of conservation. The second figurine represented a seated nursing Isis (*Isis Lactans*) ($13.5 \times 4.7 \times 6.5$) cm). Also this sample has unknown origin and was inherited by the museum from Bartolucci legacy in 1892. It is in the position of breastfeeding the baby god Horus, which is now missing. Other parts are probably missing, such as the protruding *Uraeus* over her forehead, where a square hole is visible, and two cow horns enclosing a sun disk surmounting the present *modius* adorned with *Uraei*. A tang underneath the legs would have been used to secure the statuette to a base. The surface of the bronze figurine appeared completely covered by a dark almost black patina with large area of reddish corrosion products. Moreover, some traces of gilding were visible on the face and in the two parts of the finely engraved wig falling onto the chest. Ancient Egyptian black-patinated copper alloys has attracted much attention in the last century and the debate on their production process is still open [13,15,16,26,27]. We will address this issue later. The last figurine represents a seated Neith ($13.5 \times 3 \times 5$ cm), warrior goddess, wearing the red crown of the Lower Egypt. Two tenons, one under the legs and one under the feet, were probably inserted into a missing throne. Its provenance was not known and was acquired by the museum in 1824 from the private Nizzoli collection. The left arm was broken but the surface of the figurine appeared well preserved, with limited corrosion phenomena. The three bronze figurines were stylistically dated to the Late Period (664–332 BC).

Neutron tomography was performer at the imaging facility CONRAD II at the Hahn–Meitner research reactor at Helmholtz-Zentrum Berlin (HZB) [28,29]. The cold neutron beam (wavelength range 1.5 Å–10 Å with peak at 2.5 Å) is directed to the tomography setup via a curved neutron guide which provides a flux density of about 2×10^9 n/(cm^2 s). Beam collimation was performed by means of pinhole geometry with a 3 cm diameter circular pinhole resulting in a beam collimation ratio (L/D) of 333. A conventional 100 μm thick 6LiF:ZnS scintillation screen has been used along with a CCD camera with 2048×2048 square pixels (size of 13.5 μm). The imaging setup allowed achieving a spatial resolution of about 200 μm with a field of view (FOV) of 20×20 cm and an effective pixel size of 107 μm. The sample was rotated stepwise around a fixed vertical axis (500 steps for 360° rotation), whereby for each rotation angle a projection image was recorded with exposure time of 50s. The set of projections have been processed by commercial reconstruction software in order to obtain the 3D distribution of the attenuation coefficients in the investigated sample volume.

The time-of-flight neutron diffraction experiments have been performed on the Italian Neutron Experimental Station (INES) [30], situated at the ISIS spallation neutron source of the Rutherford Appleton Laboratory, UK. INES diffractometer is equipped with nine detector banks covering 2θ angles from 20° to 163° in the horizontal scattering plane. Neutrons scattered by the sample produce nine separate diffraction patterns (partially overlapping) each of them covering a different d-spacing range with different resolution. The incoming neutron beam of 34×34 mm^2 was shaped as shown in Fig. 1 using adjustable jaws and beam monitoring device in order to select specific region of interest for the analysis and the acquisition time was in the range 1–3 h for each measurement. Let us point the attention to the fact that TOF-ND measurements on extended object like these hollow bronze figurines are subjected to some systematic effects which could make the quantitative phase analysis quite problematic. For an extended object, the incident beam will diffract from different materials that may be located at different positions along the incident beam path. The diffraction data obtained from hollow closed sample are effectively being produced from the interaction of the neutron beam with the walls of the sample, displaced with respect to the centre of the diffractometer in the direction of the beam, resulting in two diffracted peaks, one from each side of the sample. The resolution of the instrument is sufficient to

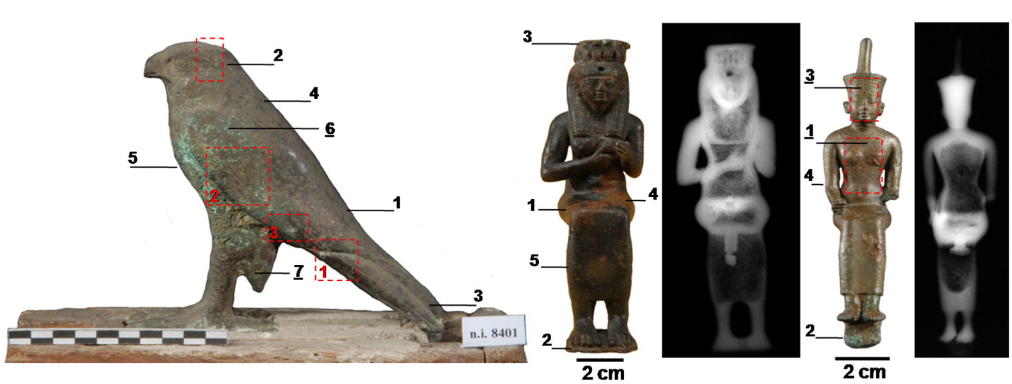

Fig. 1. Bronze figurines analyzed in this work. Left: Horus falcon (inv. 8401). Middle: Isis Lactans. Right: Neith. Dashed squares mark the TOF-ND analysis. LIPS measurements are numbered for each sample and underlined numbers indicate measurements done on the backside. The shown X-radiographies have been performed at 220 KV, 6 mA and 90 s of exposure time.