Characterisation and Analysis of Metallic Artefacts from the Pylos Archaeological Museum

M. Kylafia, A. Katakosa, S. Boyatzis, E. Palamara and N. Zacharias

ABSTRACT
The present study focuses on the analysis of four unique artefacts, originally recovered from a tomb complex of the Hellenistic period and now displayed at the New Pylos Archaeological Museum, Niokastro fortress of Pylos, Greece (since 2016). The items are rod-shaped, with lengths between 5.5 and 14.6 cm and intricate decorative patterns. The rods were analysed following a multi-technique, non-invasive approach, using optical microscopy, XRF, SEM/EDS and FTIR. The analysis suggests that the three brown rods are made of wrought iron; successive areas of calcite crystal formations are associated with environmental depositions and corrosion defects. The white rod shows distinctly different chemical characteristics: it is composed of a thick core identified as bone and covered by a thin layer of lead.

The combined microscopic, chemical and spectroscopic analysis resulted in the chemical characterisation of the artefacts and thus in a better understanding of their properties. In turn, the analysis has lead to hypotheses for the likely function of these unique artefacts (i.e., three writing implements and one decorative hinge).

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Introduction
During the relocation works of the Archaeological Museum of Pylos at the Maison Building in the Niokastro fortress of Pylos, in Messenia, Peloponnese (a project carried out by the Ephorate of Antiquities of Messenia (2013-2015) and co-financed by Greece and the European Union) archaeometric analyses were carried out on a unique group of artefacts to provide information regarding their preservation state, raw materials, manufacturing technology and likely function. The four selected artefacts present unique forms and decorative patterns, while their intended function was undetermined. Taking into consideration that these artefacts were placed inside a wealthy burial complex alongside other valuable offerings, their more detailed analysis presented particular interest. At the same time, significant analytical problems were posed due to the complex structure of the artefacts and the fact that sampling was not allowed.

Archaeological samples
The present study focuses on the analysis of four unique artefacts recovered from a five-graves complex excavated in 1962 and 1965 by G. Papathanasopoulos and colleagues at the site of Tsopani Rachi near the modern village of Tragana in Pylos, Messenia (AD 17 (1961-62); AD 18 (1963); AD 21(1966)), dated to the Hellenistic period (3rd – 1st c. B.C.).

The specific finds come from the cist grave (T.3) that shared the same long side wall with the neighboring grave (T4) (Figure 1). The graves provided several burials accompanied with an enormous number of offerings, such as vases of the ‘West Slope Ware’ decoration, bronze mirrors, lead pyxis, iron strigils, bronze and iron nails and lead parts related to the presence of wooden box, spindle hooks, a clay vase bearing the inscription AAYIOY (referring either to the medicine alypon or the pharmacist Alypos). The number and luxurious nature of the recovered offerings highlighted the significance of the burial complex in the archaeological record.

The four items are rod-shaped, with a varying length of 5.5, 7.5, 12 and 14.6 cm and present intricate decorative patterns. Three of them are of brown colour and one has a whitish external surface and presents two pierced holes (Figure 2 and Table 1).

Methodology
The 4 rods were studied using a multi-analytical approach in order to determine the raw materials, manufacturing technology and preservation state, aiming at subsequent determination of their original function. Due to the unique character of the samples,
particular care was taken to apply only non-destructive techniques.

Optical microscopy using a fibre optics system (FOM/i-scope, Moritex) was performed on all samples aiming at the detailed documentation of the complex decorative patterns. Moreover, the microscopic observation enabled an initial examination of the preservation state, as well as the structure of the samples.

An initial in-situ chemical examination of the samples was conducted at the Museum using portable X-Ray Fluorescence (p-XRF) analysis. The advantages of this technique for the non-invasive in-situ analytical characterisation of cultural heritage artefacts is well documented (Liritzis and Zacharias, 2011). The analysis was carried out with a portable Bruker Tracer III SD set up, with a beam diameter of 3 mm. The setting used was an Al/Ti filtered (0.012 inches Al plus 0.001 inches Ti) high-energy excitation mode (high voltage set at 40 kV and current of 12 μA) and the collection time of each measurement was 120 sec (Palamara, et al., 2016). The acquired data were only used qualitatively, due to the multi-layered structure of the samples, which was noted by the microscopic examination.

For the better evaluation of the structure and composition of the samples, they were analysed by Scanning Electron Microscopy coupled with an Energy Dispersive Spectrometer (SEM/EDS). The rods were initially placed in the SEM chamber, mounted with the aid of a carbon tape and analyzed under a SEM type JEOL JSM–6510LV coupled with an Oxford Instruments EDS (Moropoulou, et al., 2016). The analytical data were obtained by INKA software. The bulk analyses were conducted at high vacuum, 20 kV accelerating voltage and with a count time varying between 100 and 300 sec.

During the conservation process, micro-samples, easily detached from the core and the exterior surface were taken from each artefact. These micro-samples were analysed by SEM/EDS using the same settings as the intact objects, without any prior preparation.

Selected micro-samples were additionally analysed by Fourier Transform Infrared Spectroscopy (FTIR) to further investigate the materials in the artefacts. Powder micro-samples from the surface of metal rods A, B and C were pressed in the form of KBr discs and their FTIR spectra were accordingly recorded (20 scans, 4 cm-1 resolution) using a Perkin-Elmer Spectrum GX I FTIR system (Perkin-Elmer, Waltham, MA USA).

Table 1. Basic morphological characteristics of the 4 rods under study.

| Sample | Length (mm) | Width (mm) | Colour | Surface |
|--------|-------------|------------|--------|---------|
| A      | 14.6        | 3-4        | Brown  | Decorative patterns, corrosion effects |
| B      | 12          | 3-4        | Brown  | Decorative patterns, corrosion effects |
| C      | 7.5         | 4          | White  | Smooth surface, 2 symmetrical holes |
| D      | 5.5         | 3-4        | Brown (with white areas) | Decorative patterns, corrosion effects |
Optical microscopy

The observation of the samples via a LED microscope suggested in all cases the likely presence of multiple layers, made of both organic materials and metal. In the case of samples A, B and D, which present intricate decorative patterns, it was suggested that the rods were originally decorated and wrapped by organic materials, which are now mineralized, such as rope, threads or skin strips. These organic materials were probably held in place by a metal ring. Below, a group for FOM images is given, documenting their preservation state and morphological characteristics (Figure 3).

XRF analysis

The XRF analysis of the four samples showed that the metal section of samples A, B, and D is almost pure iron, with very low concentrations of impurities (Figure 4). On the contrary, the metal layer of sample C is primarily made of lead, with lower concentrations of iron, copper, zinc and manganese (Figure 4). It should be highlighted that sample D was originally considered similar to sample C, based on its colour; it shows however the same chemical traits with the two brown samples (A and B). The lighter colour of its surface can be attributed to corrosion effects on the external surface of the rod.

SEM/EDS analysis of intact rods

The SEM/EDS analysis of the lead rod (sample C) revealed the presence of two distinct parts: a core and an outer layer (Figure 5). The core is thick and smooth and was probably made of one elongated organic item. Based on its chemical composition, containing carbon, calcium and phosphorus, the organic material could probably be attributed to bone. The core is covered by a thin layer of silicon and lead. The diameter of the two apertures of the rod was measured equal to 2.1 mm and 2.43 mm respectively (Figure 6).

The SEM/EDS analysis of the three intact iron rods did not lead to any clear conclusions regarding the structure of the rods or the composition of each layer, though areas of iron and a calcitic material were identified. The analysis was significantly hindered by the decorative patterns and the weathering effects, as well as layers of organic material that covered parts of the external surface after previous conservation treatments. An initial hypothesis was made, according

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**Figure 3.** FOM images (x50) from artefact A, showing 3 characteristic features, also present at artefacts B and D: (left photo) surface patterns (lower part of the photo) and typical laminates of corroded wrought iron from the inner matrix (upper part); (middle photo) scaly surface patterns which point to organic decorations being mineralised; (right photo) a central pattern indicating the shape of a rope or skin strips decoration and (upper part) a flat area possibly associated with the existence of a metal ring.

**Figure 4.** Representative XRF spectra of the metal layer of the brown samples (A, B, D) (left) and of the white sample (C) (right).
to which the rods are made of an iron core which is covered externally by a calcitic substance.

**SEM/EDS analysis of micro-samples**

The SEM/EDS analysis of the micro-samples from the lead rod (sample C) verified the previous results from the examination of the intact rod. For the three iron rods (samples A, B and D) multiple micro-samples were examined. The analysis showed that all micro-samples consist primarily of pure iron covered in areas by a calcium-rich material (Figure 7).

It is interesting to note that the parts of pure iron demonstrate characteristic porous texture (Figure 8). The Ca-rich layer contains pure Ca and C and so most likely is composed of calcium carbonate. The
crystals observed in some cases reinforce the hypothesis that the layer covering the iron is calcitic (deposited and grown on the surface) (Figure 9).

Regarding the structure of the three brown rods (artefacts A, B and D), the initial hypothesis of an iron core covered by a calcitic layer was rejected based on the chemical mapping of micro-samples representing cross-sections of the rods. As shown in Figure 10, large areas of the cross-section consist of pure iron. Calcium, however, is not only present in the outside surface, but in distinct layers throughout the cross-section. It seems therefore that the three brown rods are in fact made solely out of wrought iron which characterize iron objects from the Hellenistic period. Based on the morphology of the micro-sample of Figure 10, the presence of calcite can be attributed to the precipitation of carbonates (mainly calcite and in other cases, also siderite) from underground waters filling internal gaps or cracks in the iron body. Large scratches are visible throughout the surface of the rods, as for example can be seen in Figure 10. Similar patterns have been mentioned in the literature at similar studies (Angelini, et al., 1998; Neff, et al., 2004; Neff, et al., 2005).

**FTIR analysis**

FTIR analysis of micro-samples from the lead rod (sample C) corroborated the presence of bone (Figure 11). In the resulting spectra, the following components were identified: (a) phosphates, in the form of hydroxyapatite, with bands at 565, 604 and 1033 cm$^{-1}$ (Newesely, 1989; Koutsopoulos, 2002; Leventouri, 2006; Antonakos, et al., 2007); (b) calcium carbonate, CaCO$_3$, with bands at 710, 873, 1421, 1499 and 2516 cm$^{-1}$; and (c) collagen.
in deteriorated state, with maximum at 1567 cm$^{-1}$ and shoulder at 1656 cm$^{-1}$ (amide II and I, respectively). Collagen index ($A_{1650}/A_{1033}$) was found as low as 0.21, suggesting significant mineralization, while crystallinity index ($[A_{605}+A_{664}]/A_{590}$) was found relatively high (3.37) suggesting diagenetically altered bone in which dissolution and recrystallization of phosphates led to crystal size increase (Weiner, 2010; Surovell and Stiner, 2001; Rey, et al., 1991; Hedges, 2002; Thompson, et al., 2009).

It is important to highlight that the only siliceous material identified alongside lead in the outer surface of Sample C is characterized as phytogenic. Therefore, the presence of Si should be attributed to environmental depositions and not to an intentional addition to the outside lead layer.

Figure 11. Representative FTIR spectrum of micro-sample from the lead rod (sample C).

The analysed micro-samples from the other three rods present primarily inorganic material and especially iron minerals (Figure 12). The main iron minerals present in all spectra are iron hydroxy-oxides and magnetite: (a) goethite ($\alpha$-FeOOH), with characteristic bands at 405, 465, 800 and 877 cm$^{-1}$; (b) lepidocrocite ($\gamma$-FeOOH), with a characteristic band at 1020 cm$^{-1}$; and (c) magnetite ($\text{Fe}_3\text{O}_4$), with a

Figure 12. Representative FTIR spectrum of the micro-samples from the iron rods (samples A, B and D); calcite bands majorly overlap iron hydroxy-oxide bands.
characteristic band at 613 cm\(^{-1}\) (Cornell and Schwertmann, 2003; Ruan, et al., 2001; Ruan, et al., 2002). The presence of lepidocrocite is indicative of extensive weathering of the iron (Oh et al. 1998). The same applies for goethite, which is a result of the chemical transformation of lepidocrocite over time (Ramana et al. 2007).

At the same time, calcite is the only carbonate identified clearly in all spectra (with characteristic bands at 713, 877, 1425, 1800 and 2517 cm\(^{-1}\)), thus verifying the results of the SEM/EDS analysis (Wijnja and Schulthess, 2001; Gunasekaran and Anbalagan, 2008; Elliott, et al., 1985).

Finally, weaker bands at 3408, 2862, 2921, 3143 and 1741 cm\(^{-1}\) were detected, assignable to organic material, possibly due to unspecified fatty substances, as well as amines (typical corrosion inhibitors possibly due to previous conservation treatments); the latter was further supported through subtraction of intense overlapping calcite infrared peaks, clearly showing typical broad amine bands with maxima at 3140 and 1585 cm\(^{-1}\) (not shown) (Coates, 2006; Shurvell, 2006). The identified organic material should be attributed to corrosion effects caused by its burial environment.

Conclusions

The combined use of non-invasive and robust micro-destructive analytical techniques can shed light towards the characterization and use of archaeological artefacts and stand as a prerequisite during restoration and museum studies. The scientific analyses of the four artefacts presented in this paper provided valuable information which is now used to enhance and promote the significance of the tomb complex within the settings of the new Archaeological Museum of Pylos.

The analysis of the four rods presented here was particularly complicated, primarily due to the complex structure of the artefacts, the poor preservation state, the inability to cut off micro-samples, as well as the fact that they had undergone conservation treatments in the past. The multi-analytical and non-invasive approach that was used included both in-situ and laboratory techniques and proved successful for the archaeometric analysis of the artefacts; the main outcomes of each technique are summarized in Table 2.

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Disclosure Statement

No potential conflict of interest was reported by the author(s).

ORCID

S. Boyatzis  http://orcid.org/0000-0001-9237-041X

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