[title]New Results on the Alloys of the Croatian Apoxyomenos

[author]Iskra Karniš Vidovič

[affiliation]Hrvatski restauratorski zavod (HRZ: Croatian Conservation Institute), Zagreb, Croatia [author]Benoît Mille

[affiliation]Centre de Recherche et de Restauration des Musées de France (C2RMF), Paris, France

[A-head]Abstract

[abstract]

Following the cooperation initiated in 2012 between the Croatian Conservation Institute (HRZ) and the Centre de Recherche et de Restauration des Musées de France (C2RMF), the two institutions furthered their common investigation of the Croatian Apoxyomenos, a bronze male statue of the second or first century BC found in the sea in 1999. A new set of metal analyses was performed in order to clarify the alloy composition of the statue. In previous analytical campaigns, problems were encountered due to the heterogeneity of the metal and the heavy corrosion of the statue. We concluded that for a correct determination of the metal composition, a larger sample size was required. In addition, great care had to be taken to avoid inclusion of corrosion products in the samples, and that sample locations had to be chosen according to the results of a detailed investigation into the manufacturing technique of the statue.

**[A-head]Introduction**

[main text]

The statue of an Apoxyomenos (**fig. 43.1**), raised from the Adriatic Sea off Croatia in 1999, has been thoroughly restored and investigated at the Croatian Conservation Institute (HRZ). It has been exhibited in Zagreb, Osijek, Rijeka, Split, and Zadar in Croatia, as well as in Florence, Ljubljana, Paris, London, and Los Angeles. Results of conservation-restoration works and investigations have been published and presented at several conferences, including international congresses on ancient bronzes in Bucharest (2003) and Zurich (2013).

In 2012, during the exhibition of the statue at the Louvre, the HRZ established a cooperation with that institution leading in 2013 to new insights into the technology of the Croatian Apoxyomenos,[[1]](#endnote-1) and continuing in 2015 with a new campaign to analyze the alloys used to produce the statue.

**[A-head]Alloy Investigation Prior to 2013**

After the statue had been raised from the sea in 1999, and before its conservation, the most important tasks were to determine its state of preservation, to prepare it for transport to the HRZ in Zagreb, and to determine a conservation methodology. Therefore, while it was still on the island of Lošinj in 1999, µ-radiography with an iridium-192 source was performed, using a portable device. This process yielded images that not only showed problematic areas on the statue, such as fractures and lacunae, but also illustrated the technique by which the statue was manufactured.

The conservation treatments and research performed at the HRZ in Zagreb in cooperation with the Opificio delle Pietre Dure (OPD) lasted for six years until 2006.[[2]](#endnote-2)

Already in 1999 more than a hundred different samples were collected from the interior and exterior of the statue. However, the amount of metal in these samples was very small and mostly included corrosion products.

After a first and necessary desalination, several sampling and analytical campaigns were conducted between 1999 and 2003, by taking metal samples and by performing surface analyses during the conservation-restoration treatments. The aim was to provide information about the elemental composition of the alloys used for primary and secondary castings (including welding and repairs), soldering, patches, and inlays.

In the first phase of sampling between 1999 and 2002, during the initial conservation treatment, some 43 samples were analyzed at the Scientific Laboratory of the OPD (14 metal fragments, 9 solder and welding alloys samples, 20 samples of corrosion products and crystals on the internal and external surface of the bronze; **fig. 43.2**).

The metal structure in the samples was found to be very heterogeneous and spongy, showing penetration of corrosion into the bronze wall on both sides (interior and exterior), especially on the rear of the statue that had been buried in sand on the seabed. Experts from the OPD performed several analyses to examine the samples, using stereomicroscopy, stratigraphic investigation under an optical microscope, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDS), and inductively coupled plasma atomic emission (ICP-AES).

The most significant and interesting analyses and results were provided by ICP-AES and SEM-EDS, which were performed in parallel for some samples. For ICP-AES, the entire samples were dissolved in acid mixtures at the temperature of 350°C, meaning that they included “deteriorated” areas. The results showed that the bronze alloy is highly leaded.

Since lead appears concentrated in globules of 50–200 μm and in surface areas, SEM-EDS was preferred, and only sound areas deep in the samples were investigated. Only very small areas (500 μm² or even only 100 μm²) were analyzed in the samples. SEM-EDS only gave results for major elements, but they showed a very different metal composition, with a low percentage of lead in the bronze alloy.[[3]](#endnote-3)

In addition to the analyses performed by the OPD before 2003, further analyses were performed by the Ruđer Bošković Institute in Zagreb and by the HRZ, based on 5 samples and applying PIXE spectroscopy. Again, the samples were heterogeneous and only one—sample no. 5859, taken from the interior of the chin—gave results similar to the ICP-AES analyses:

[unnumbered list]

Cu 76.4% (58.9–92.5%)

Sn 7.1% (4.7–8.5%)

Pb 16.1% (2.12–32.1%)

Si 0.19% (0.14–0.26%)

Cr 0.01% (0.0–0.2%)

Fe 0.13% (0.7–0.17%)

Ni 0.03% (0.0–0.6%)

[end unnumbered list]

In 2003, after the complete removal of the calcareous encrustations from the statue, a second campaign of investigation was carried out by the HRZ and the Ruđer Bošković Institute, applying three different analytical techniques based on X-ray: portable XRF spectrometry (70 points), external beam PIXE (same areas as XRF) and micro-PIXE using the Zagreb proton microprobe facility. These tests yielded elemental maps on cross sections obtained from two selected samples (head and right leg).

The X-ray surface analysis proved to be not representative of the bulk alloy, showing a heavily corroded surface with large discrepancies in element concentrations, thus indicating that such measurements could not estimate the original metal composition. X-ray maps on cross sections showed a typical structure of high-lead bronzes, but also that corrosion deeply affected the metal walls on both sides, up to the depth of 600 μm.[[4]](#endnote-4)

In all of these prior investigation methods and procedures, the main problems preventing a correct determination of the elemental metal composition were metal heterogeneity, especially as regards the lead distribution, and the heavy corrosion of the statue. SEM-EDS analysis was unable to ascertain the lead level since only a volume of 0.5 mm3 (at the most) had been analyzed. Furthermore, SEM-EDS is not sensitive enough to detect trace elements. ICP-AES analysis was unfortunately performed on samples including “deteriorated” areas and at a very high temperature for sample digestion, leaving some doubt as to the obtained results. Given the thickness of the corroded bronze walls, surface analyses by XRF or PIXE never reached a sound metal composition. PIXE maps and other techniques based on metallographic sections required large samples, which could not be taken in significant numbers given the damage they cause to the statue.

**[A-head]Re-examination of the Manufacturing Techniques (2013)**

As noted above, we concluded that for an accurate determination of the metal composition, and especially the lead level, a “volumic” method was required. We also knew that great care had to be taken to avoid inclusion of corrosion products, which can strongly bias the results. But these conditions are not sufficient: before choosing appropriate locations for new samples, a comprehensive technological understanding of the statue was also needed. A re-examination of the manufacturing technique of the statue was therefore undertaken: How many separately cast sections (primary castings) are there? Where are the joins located? Were the sections soldered or welded? Where and how was the statue repaired?

Our examination confirmed that the statue had been produced by an indirect lost-wax process. It is a hollow cast; that is, the casting core was removed and only minor traces of it remained. Hence the total weight of the statue is only about 125 kg, making it easily transportable.

The statue is made of seven main parts (head, torso, legs, arms, and genitals). Arms, legs, and genitals were joined to the torso by flow fusion welding. The head was soldered onto the neck. The plinth parts were also soldered together and the feet were then soldered to the plinth (**fig. 43.3**).

The head was cast in one piece, with a bronze wall 5 to 8 mm thick. A large casting defect under the left eye was repaired by a secondary casting; smaller rectangular patches closed the core pin holes. The head-to-neck join has a very typical path with right-angle corners below the ears and platforms between the head and the neck in order to accommodate the soldering. The eye inserts are unfortunately lost but the lips are still there. They are made of unalloyed copper that was inserted into rectangular mounting channels, and finally hammered in place.

The torso is interesting for visible traces of manual work on the wax from the inside, in the mold. Here also, the bronze wall thickness ranges from 5 to 8 mm. There are copper inlays also for the nipples, hammered into shallow round recesses cut into the bronze surface.

The legs show different thicknesses of the bronze wall: 4–6.5 mm for the right leg and 8–11 mm for the left. They were cast in an upright position and the majority of the casting defects, caused by massive gas emission, are visible in their upper parts. The right leg in particular shows that repairs to the cast leg as well as in the welding area were made using multiple patches—both smaller rectangular ones and larger polygonal ones.

The hands were joined to the arms by a wax-to-wax method. Some of the fingers were cast separately. The small finger of the left hand is lost and the interior of the left hand is accessible through the hole only at this point, since the hand-to-arm join is closed on the left side. On the right side, however, it is open.

Before assembly, the casting core was removed from all parts of the statue. The statue was joined in five phases: (1) the arms to the torso; (2) the complex leg area (first the right leg, then the left); (3) the pubic area and genitals; (4) soldering the head onto the neck; and (5) soldering the feet onto the plinth. Joins 1–3 were performed using a flow fusion welding technique in basins for legs and arms (secondary castings of bronze). All welding areas had to be repaired with multiple patches.

All joins and repairs are now easily followed thanks to γ-radiography, the archeological drawings (**fig. 43.4**), and new X-ray images made by the C2RMF (complete frontal and profile views).[[5]](#endnote-5)

This re-examination confirmed that the Croatian Apoxyomenos is a typical product of the Late Hellenistic period,[[6]](#endnote-6) though the original prototype is dated to the mid-fourth century BC according to stylistic features.[[7]](#endnote-7)

**[A-head]New Sampling Campaign (2013–2015)**

Taking into consideration the previous metal analyses and our better understanding of the casting and welding techniques, we decided to perform additional analyses using ICP-AES. Seven new samples were taken by microdrilling (**fig. 43.5**), some of them from the previously examined areas: 6 from primary castings (head, body, foot, pubic hair, decorated plinth, undecorated plinth) and 1 from a weld join (the pubic area onto the legs and the body area).

Analyses were performed by ICP-AES at the C2RMF. About 20 mg of metal was taken for each sample (1 mm diameter, 10 mm deep) after eliminating most surface corrosion products. The drillings were carefully controlled under the stereomicroscope to avoid any corrosion product or dust. About 10 mg of the drillings were precisely weighed and digested in 5 ml aqua regia solution (hydrochloric and nitric acids). The solution was then nebulized in the argon plasma and 29 chemical elements were quantified.[[8]](#endnote-8) The detailed results of the ICP-AES analyses can be found in **table 43.1**.

By using this analytical procedure, we achieved a very consistent new set of results. Regarding major elements, we observed that the same alloy has been used for the primary castings of all parts of the statue, including the undecorated rear face of the plinth (**fig. 43.6**). It appears that the alloy of the Croatian Apoxyomenos is a highly leaded bronze (Sn 6.7 ± 1.9%; Pb 18.0 ± 4.0%); this alloy was also used for welding. A noticeable exception is the decorated side of the plinth, showing higher tin contents and lower lead (Sn 9.5%; Pb 11.0%).

Furthermore, all high-lead bronze parts share the same trace-elements pattern (**fig. 43.7**), and confirm that they are made from the same copper: a typical 0.1% level of silver, arsenic, and antimony and about 0.03 % nickel. One notable discrepancy is in the iron and zinc levels. As these two elements are very easily oxidized from bronze in the liquid state, a possible explanation could be a delayed casting for some parts of the statue, i.e., some liquid metal was left at high temperature for too long, thus leading to some oxidation of the metal batch.

Very interesting is the fact that the corresponding impurities pattern is not only consistent for all parts of the statue itself, but also for the undecorated side of the plinth. We can therefore deduce that this part of the plinth was cast at the same time as the rest of the statue.

Given the distinct alloy of the decorated plinth face and its lower impurities pattern (Ag/Bi/Sb only), it is very likely that the decorated parts of the plinth were manufactured in a later phase. It seems possible that a major restoration and/or modification of the plinth occurred already during the ancient life of the statue.

[A-head]Bibliography

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1. Karniš Vidovič and Mille 2015. [↑](#endnote-ref-1)
2. Karniš and Domijan 2006, Michelucci 2006. [↑](#endnote-ref-2)
3. Lalli et al. 2006. [↑](#endnote-ref-3)
4. Mudronja et al. 2010. [↑](#endnote-ref-4)
5. See Karniš Vidovič and Mille 2015, figs. 3–4. [↑](#endnote-ref-5)
6. Karniš Vidovič and Mille 2015. [↑](#endnote-ref-6)
7. Cambi 2006. [↑](#endnote-ref-7)
8. The operating conditions are described in Bourgarit and Mille 2003. [↑](#endnote-ref-8)