LABORATORY INVESTIGATION OF INLAYS AND SURFACE TREATMENTS FOR THE DECORATION OF COPPER-BASE ALLOY OBJECTS FROM THE IMPERIAL ROMAN PERIOD

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1. INTRODUCTION

Metal polychromy has been widely used for the decoration of metallic artworks from the far antiquity. In the Hellenistic and Roman periods, the famous Corinthian bronzes (*Corinthium aes*) are a typical example of the skill of metallurgical craftsmen working in their aim to obtain coloured surfaces on copper-based alloys [Craddock 1993].

The present paper summarises a full characterisation study of three metallic objects from the Imperial Roman period kept in the Department of Greek, Etruscan and Roman Antiquities of the Louvre Museum: an inkpot, a strigil, and a bistoury handle. This investigation is aimed to a re-evaluation of the techniques of metal polychromy at the Imperial Roman period, as a part of a general study concerning the identification and understanding of the technical history of artificial surface treatments (patination) and inlaying on copper-base archaeological pieces of art.

The objects and their inlays and surface treatments have been studied by optical microscopy, X-ray radiography, elemental analysis by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) and PIXE (Particle Induced X-ray Emission), X-ray diffraction, RBS (Rutherford Backscattering Spectrometry), micro-Raman spectroscopy. All the results are discussed with reference to the scarce existing texts which describe the techniques of metal colour modifying in the antique Roma.

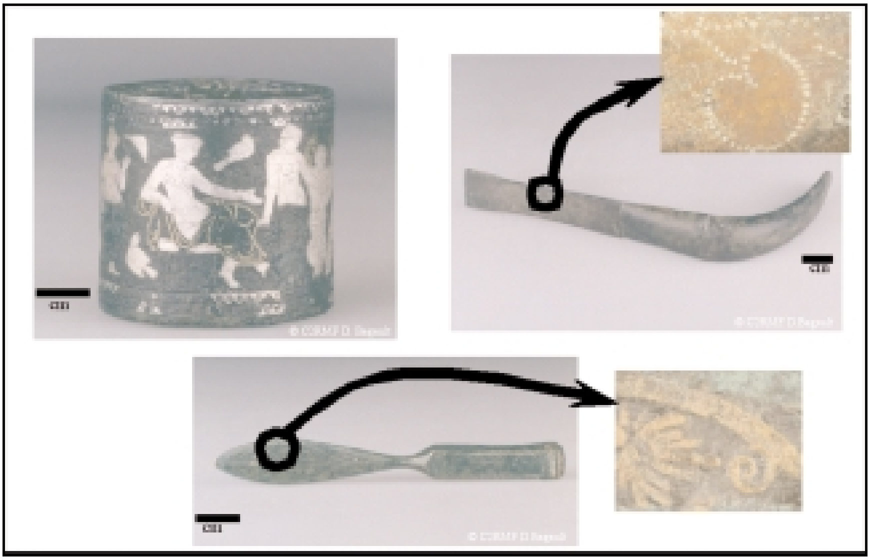

Figure 1. Objects from the Department of Greek, Roman and Etruscan Antiquities, Louvre Museum (1st – 2nd century AD). © C2RMF, D. Bagault.

2. THE OBJECTS

The three Roman Empire objects (fig. 1) are all dated from the Ist or IInd century AD:

— An inkpot (inv. Bj 1950), inlaid with various metals on a corroded background;

— A bistoury handle (inv. Br 2516), decorated with black and red inlays on a corroded background;

— A strigil (inv. Br 1582), decorated on a corroded background.

The inkpot is known since 1876 without any precise date and context of discovery; it was acquired by the Louvre museum in 1883 [Héron de Villefosse 1878]. The scene represents the goddess Venus with her entourage: Psyche, Adonis, a servant and several Eros. This kind of inkpot, functional and precious, decorated with figures, is very rare; apart from this one, only three complete are known: one in the museum of Alger (found in a tomb at Lambèse) and two in the British Museum; some inkpot covers are also known such as those from Mainz, Cologne or Volubilis.

The origin of the bistoury handle is uncertain. The iron blade has disappeared.

The strigil was found in the necropolis of Sicca Veneria, nowadays Le Kef in Tunisia, and given to the Louvre museum in 1895 [Denis 1894]. Part of the handle decoration is punctured: on one side, the figure of a wrestler running to the right, on the other side, stalk and ivy leaves. These designs appear in-between chessboard-like patterns.

All artefacts show metallic inlays and/or patinated regions: the inkpot and bistoury handle are inlaid with black inlays (Venus and Adonis himations on the inkpot, the symmetrical decoration on the bistoury handle); the strigil exhibits regions (fig. 1) with a different colour and surface state than the neighbouring areas.

3. INSTRUMENTATION

After optical microscope observation, X-ray radiographs were done (100 kV, 4 mA, Pb screen); to obtain a lisible radiograph of the inkpot body, a special procedure had to be developed to avoid superposition [Borel 2004]. Bulk metal analysis of each object was performed on metal chips obtained by micro drilling with a 1mm drill; the sorted metallic chips are digested in acid to be analysed by ICP-AES [Bourgarit 2003].

The surface analyses had to be entirely non-destructive. Ion beam analyses were performed by using the external beam of the particle accelerator AGLAE, a 4 MV tandem accelerator delivering a proton or alpha particle beam of high energy, extracted to free atmosphere through a 100 nm thick Si_3N_4 window [Dran 2000]. The analysed spot is of 50 mm diameter. X-ray emission under 3 MeV protons or 6 MeV alpha particles allows PIXE quantitative analysis [Dran 2000]. Backscattered particles under 3 MeV protons or 3 or 6 MeV $^4He^{++}$ particles are used for RBS analysis, which allows in-depth profiling of the elemental concentrations over a few μm [Ioannidou 2000]. The RBS spectra are interpreted thanks to the SIMNRA code [Mayer 1997-98].

The surface crystalline compounds were identified by diffraction in an X-ray diffractometer equipped with a Co Kα tube (40 kV, 40 mA) and focusing mirrors.

The surface compounds were investigated by micro-Raman spectrometry (Jobin-Yvon Infinity equipped with CCD detector, notch filters and a

Figure 2. X-ray radiographs of the inkpot. Left: top; right: unrolled body © C2RMF, T. Borel.

horizontal issue); the incident beam is a (Nd:Yag) laser (532 nm, 12 to 5 μW); spatial resolution is down to 2 mm.

4. RESULTS AND DISCUSSION

4.1. Radiography of the inkpot

The inkpot X-ray radiographs (fig. 2) reveal its fabrication by casting in three parts: the body, the top and the bottom, soldered afterwards. They evidence the sophisticated inlaying work. On the top, holes are managed to receive the butt hinge and the closing pin of the small cover presently missing.

4.2. Bulk metal analyses (table 1)

The inkpot body and the strigil are yellow brasses, whereas the inkpot top is a leaded bronze (red), and the bistoury handle is a quaternary alloy (reddish bronze colour).

Objects	Cu	Sn	Zn	Pb
Inkpot body	86	-	14	-
Inkpot top	69	6	-	25
Strigil	81	-	19	-
Bistoury handle	87	4	6	3

Table 1. Composition (wt % by ICP-AES) of the bulk metals.

4.3. Metallic inlays of the inkpot

The metallic uncorroded inlays are in gold or silver. The analyses (table 2) show that 2 different golds and 4 different silvers have been used. The reason of such diversity is partly based on mechanic constraints; but, as evidenced by the use of two different silvers for the friezes, these differences are an indication that the body and the top might have been elaborated independently. The radiographs and a peer examination of the objects showed furthermore that corroded inlays, not visible at the first sight, are present on several locations: the servant and Psyche himations, two boxes (one in the hand of Adonis, one behind the same figure), and butterfly wing figures attached to Adonis and Psyche figures. These corroded inlays show to be in pure copper (red original colour).

	Cu	Ag	Au	Pb
Venus himation gold inlay	0.40	0.12	98.61	-
Top gold inlay	0.21	1.87	95.35	-
Venus silver body	0.60	98.85	0.10	0.22
Servant silver body	0.56	98.87	0.09	0.23
Body silver frieze	4.72	93.57	0.91	0.56
Top silver frieze	3.14	95.44	0.60	0.67
Pelta-shaped base foot (silver)	2.53	95.60	0.75	0.86
Corroded inlays	> 99	-	-	< 1

Table 2. Analyses (wt % by PIXE, 6 MeV α particles) of the inkpot metallic inlays.

4.4. Patinated inlays of the inkpot

The Venus and Adonis himations are of black colour, as well as the wings of the Eros figures (fig. 3). The PIXE analysis shows that these inlays are made of a Cu-Ag-Au-As alloy (about 4 wt % Ag, 1 wt % Au, 4 wt % As, 1 wt % Pb), which could be considered to belong to the category of the "Corinthian bronze" (*Corinthium Aes*) described in the work of P. Craddock and A. Giumlia-Mair [Craddock 1993]. It is the result of the chemical attack of copper base alloys containing small amounts of gold and silver. This technique may be compared to the Japanese technique of *Shakudo* [Murakami 1993].

Figure 3. Black patinated inlays of the inkpot.

X-ray diffraction, micro-Raman spectroscopy and RBS profiling under 3 MeV protons and 6 MeV alpha particles proved that the patina is indeed cuprite Cu_2O enriched with gold and silver, as usually observed for this type of patina. It is however much thicker (more than 20 µm) than the *Shakudo* patina [Murakami 1993].

4.5. Bistoury handle inlays

Different from the bulk metal alloy (reported in table 1), the inlay alloy (fig. 1) is low alloyed copper containing (in wt %) about 0.4 % Sn, 0.3 % Pb, 0.5 % As, 0.5 % Fe and 0.3 % Ag. X-ray diffraction, PIXE analysis and RBS profiling show that the black patina is cuprite enriched with silver.

One cannot qualify these inlays as being *Corinthium aes*, because they do not contain any gold addition. This is the first observation, to our knowledge, of black patina containing silver and no gold.

4.6. The strigil patination

The strigil handle exhibits intentional red-orange coloration (inside the ivy leaves, inside the wrestler body, on the strikes of the chessboard decoration at both ends of the handle). The patina layer is constituted of cuprite and is 4.5 µm thick. It is obviously another recipe, not reported yet in the literature. This peculiar surface treatment will be discussed in a forthcoming publication [Mathis 2004].

5. CONCLUSION

These objects are new examples of the desire of roman artisans to create metallic polychrome objects as is shown in the reconstitution of the inkpot, proposed in figure 4.

The study has confirmed the roman use of "black bronze" in the pursuit of polychromy, and brought the proof of the existence of several recipes for patination: at least two kinds of alloys have been patinated in black, one containing no gold; in that case, what is the mechanism of coloration of the cuprite?

On the strigil, an artificial red patina, of red-orange colour, also made on a base of cuprite, has been discovered. It has not been reported yet in the literature.

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Figure 4. Modern reconstitution of the inkpot colours based on analytical results
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