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Micro-EDXRF, SEM-EDS and OM characterisation of tin soldering found in handle attachments of Roman *situlae* from *Conimbriga* (Portugal)

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ABSTRACT

Tin (Sn) or a Sn-rich solder applied to copper-based artefacts has been frequently used at least, since the Ancient Greece, although scarce studies have been published concerning the technology of this metallurgical joining technique.
Several filler remnants were reported to be found in a Roman collection of handle attachments of *situlae* or cauldrons (2nd century BCE–5th century CE) from the archaeological site of *Conimbriga*, a Roman city from the *Lusitania* Province (Portugal). All these artefacts were cast in high leaded coppers and bronzes.
The present study aims to contribute to the knowledge of Sn-rich soldering, an ancient metallurgical joining technique, by the characterisation of the fusible metallic alloy present in 10 Roman artefacts by means of micro-energy dispersive X-ray fluorescence spectrometry (micro-EDXRF), scanning electron microscopy with energy dispersive X-ray (SEM-EDS) microanalysis and optical microscope (OM) observations.
Results of studied solders show the presence of Cu-Sn alloys, with Sn contents ranging from δ to η phase composition (30–60 wt% Sn). As the attachments were made in leaded copper alloys, it was also observed, in some cases, the melting of the interdendritic Pb-rich chains with long-range diffusion of the solder alloy into the substrate.
The fillers compositions suggest that the handle attachments have been joined to a *situla* body by the soldering metallurgical process with Sn or a Sn-rich alloy. The studied leaded Cu-Sn attachments, probably formulated by local craftsman, were joined into the body of a *situla* or cauldron with a soft solder (soldering), a common metallurgical joint from Antiquity, although no relation was found between composition or typology and the Sn or Sn-rich solder.

1. Introduction

Soldering is a metallurgical joining technique reported to be widely used by Sumerians, Egyptians, Greeks, Etruscans and Romans [1–4]. Soldering involves the heating and fusing of a filler (metal or an alloy) with a lower melting point than the metals or alloys to be joined. In modern practice, the term soldering (soft-soldering) is applied to low-melting-point solder and brazing (hard-soldering) to high-melting-point solder [5,6]. The temperature is the main distinction between soldering and brazing. Soldering has the ability to join metals with different compositions, it is operated at low temperatures without melting the substrate (s) and it is characterised by the heating of the filler material above its *liquidus* temperature but under 450 °C. Brazing is characterised to use higher temperatures ($T > 450$ °C) [7]. These ancient joining techniques also comprise a previous aid of a flux (beeswax, borax or resin) to dissolve or disperse the oxide film of the substrate, turning on a more effective and stronger bond, after the mechanical cleaning of corrosion products from the metallic surfaces to be joined together [1,5,7–9].

Gold, silver, lead and copper-based alloys are the Ancient metals that were reported to be soldered or brazed by proper filler compositions in the *Naturalis Historia* by Pliny the Elder [4]. Gold joins were greatly examined from ancient jewelry, comprising several joining techniques and it was found that copper or a mixture of silver and copper was alloyed with gold and used for brazing [e.g. 3,8,10,11]. Lang and Hughes [5,6] analysed 19 Roman silver objects and found the presence of Cu-Sn brazing and Sn-Pb soldering, concluding that Sn-Pb soldering was mainly used to attach handles and for repairs. They also discussed the Leyden papyrus reference about the way in which the solder should

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be used, particularly the usage of tin as sticks, buttons or grains. Published analysis of lead artefacts are mainly focused on pipes for Roman hydraulic system and show the use of welding with Pb or soldering with Pb-Sn alloy [12–14]. Regarding the joining of Cu-based alloys, large bronze statues were predominantly studied for the characterisation of the ancient welding techniques [e.g. 2,15,16] and composition of the joining repairs [17]. Classical bronze statuettes from the British Museum were also examined and it was found that the soldering was made with Pb-Sn alloys [18].

Few studies have been focused so far on soldering pre-Roman copper-based objects. These include a Sn-rich corroded filler that was reported by Craddock [19] to be used to solder silver handles onto a copper bowl from Sumer; a semi-quantitative analysis performed on an early 5th century BCE Etruscan bronze plaque from the British Museum showed a solder with 90 wt% Sn, 10 wt% Pb [6]; more recently, Asderaki-Tzoumerkioti [1] presented a semi-quantitative analysis of the joining on a bronze Hellenistic urn evidencing the use of a Pb-Sn alloy for soldering the handle.

Also, in what concerns Sn or a Sn-rich solder applied during Roman times to Cu-based artefacts scarce studies have been performed. In these studies, the full characterisation of the solder alloy is absent and is being generally stated that a "soft-solder" implies the use of a Sn-Pb [2,3] or Pb-Sn alloy [20] or even indicates the use of different Sn/Pb ratios [18]. Historical sources were deeply explored by Lang and Hughes [5,6] but the interpretation of Pliny recipes assuming the word *stagnum* as tin is uncertain due to other possible interpretations of *stagnum* when it is used in soldering contexts. If *stagnum* is to be interpreted as "tin" it is confusing that in addition to *stagnum* Pliny mention tin (*plumbum album* – book XXXIII, chapter XXX [4]; [21]), "besides copper and lead, as metals that can be used for soldering" as stated by Lang and Hughes [5].

One of the reasons for the shortage of solder analysis from Cu-based alloys tableware might be the lack of filler remains in good state of conservation. Another reason might be due to geometry limitations for the analysis of the filler from intact and complete artefacts [6].

This study aims to provide an in-depth understanding of the Roman soldering practices with the characterisation of Sn-rich alloys used for soldering copper-based artefacts. To this end, a group of 10 handle attachments of *situlae* with soldering remains from the Roman archaeological site of *Conimbriga* (Portugal) was selected for elemental and microstructural study. These artefacts, originally soldered to the rim of the *situla*, were known to be used with decorative and functional purposes to hold the swinging handle of the *situla*.

Additionally, the elemental composition of one cauldron/*situla* body will be determined. The analysis of different components of the *situla* aims to evaluate probable interaction phenomena between the molten filler of the solder and the substrates (anthropomorphic attachments plus *situla* body).

The elemental characterisation of the solder alloy present in the selected artefacts was performed by means of micro-energy dispersive X-ray fluorescence spectrometry (micro-EDXRF), scanning electron microscopy with energy dispersive X-ray (SEM-EDS) microanalysis and metallographic optical microscope (OM) observations. The elemental composition of the attachments and the *situla* was performed by micro-EDXRF. Results on the composition of some of these handle attachments, cast in high leaded coppers and bronzes, have been reported in a previous work [22].

The present study also focuses on the differences and complementarity of the surface analysis techniques used and how together they can give significant contributions to the understanding of the Roman metallurgy in general and soldering practices in particular.

Fig. 1. Set of the studied artefacts: 10 handle attachments of *situlae* showing the anthropomorphic escutcheon and their respective back showing solder remnants and the situla (SIT153).